Improving the Understanding and Usefulness of Thermal Optical Carbon Analyses

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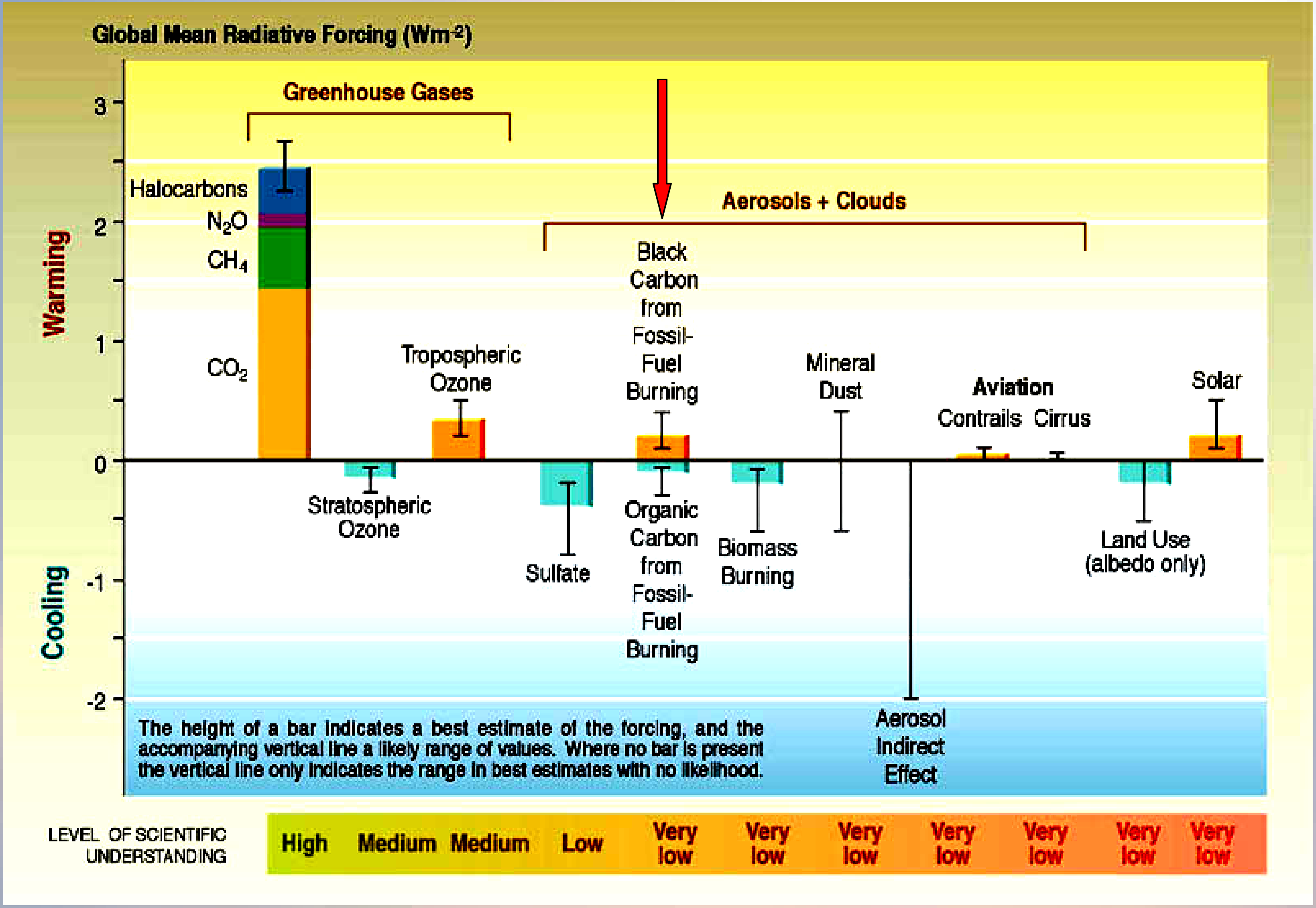
Objectives

- Provide an overview of the development of particulate carbon methods
- Summarize different OC/EC analysis methods
- Discuss research efforts to rationalize differences between common methods
- Discuss applications

Why measure particulate carbon?

- Carbon is major portion of $PM_{2.5}$
- For PM mass closure
- Carbon may have adverse health effects
- Carbon scatters (OC) and absorbs (EC) light, affecting visibility and climate
- Different sources yield different carbon fractions – useful for source attribution

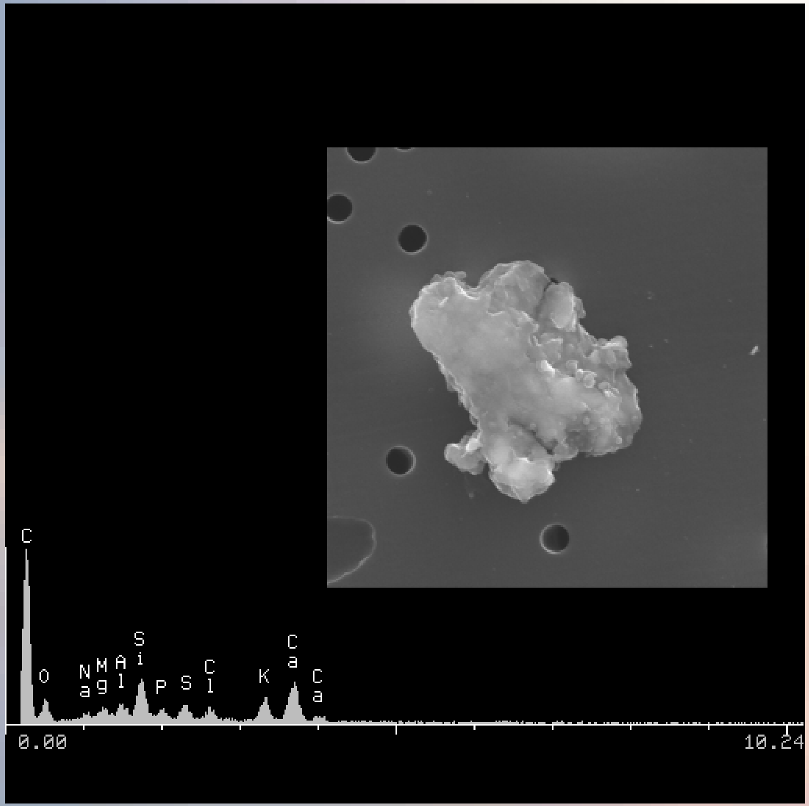
Climate Forcing by Greenhouse Gases and Aerosols



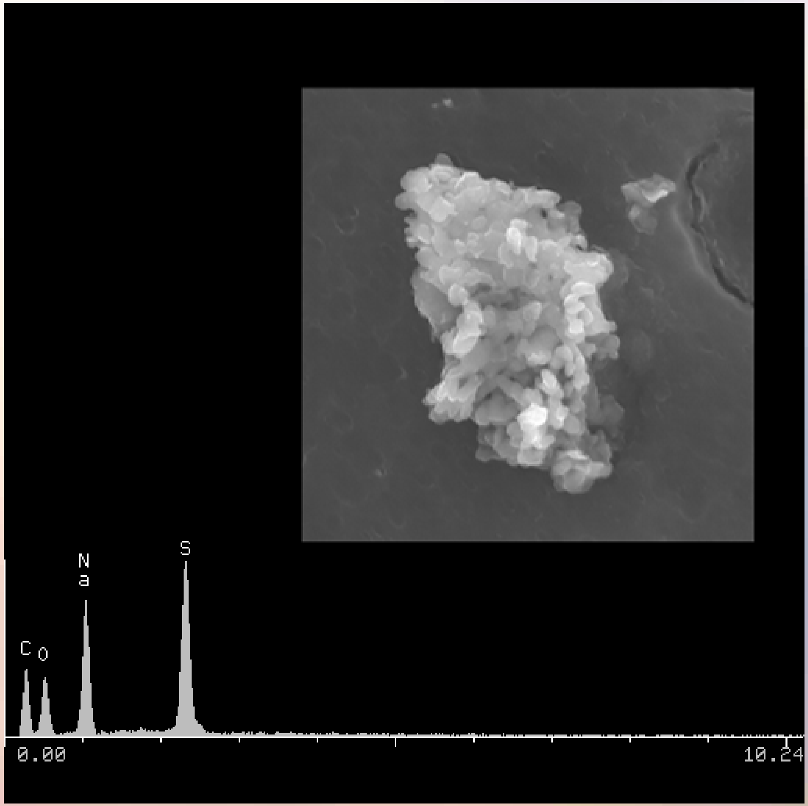
IPCC(2001). *Climate change 2001–Synthesis Report*. Cambridge University Press, Cambridge, UK.

Carbon Particles are Chemically Complex

Carbon mixed with dust



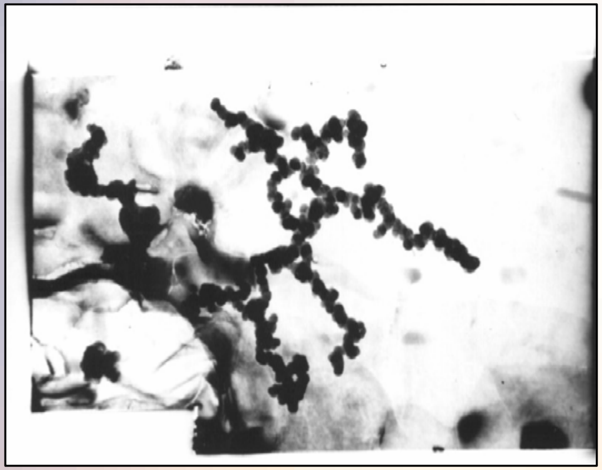
Carbon mixed with sulfur and sodium

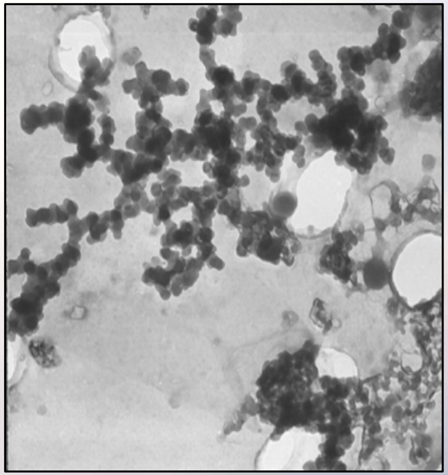


Carbon samples are optically complex

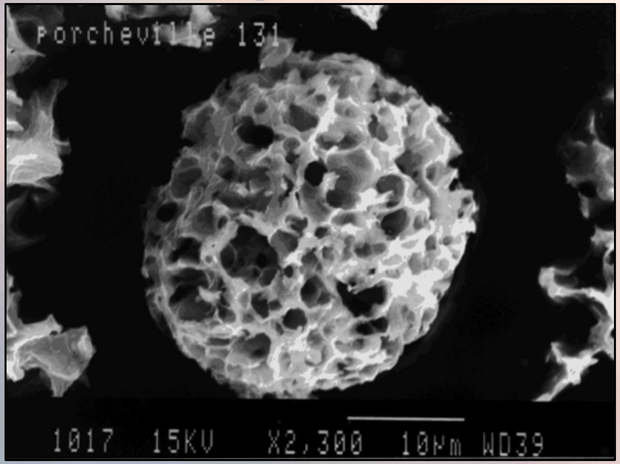
Carbon Particles are Morphologically Complex

Fresh diesel



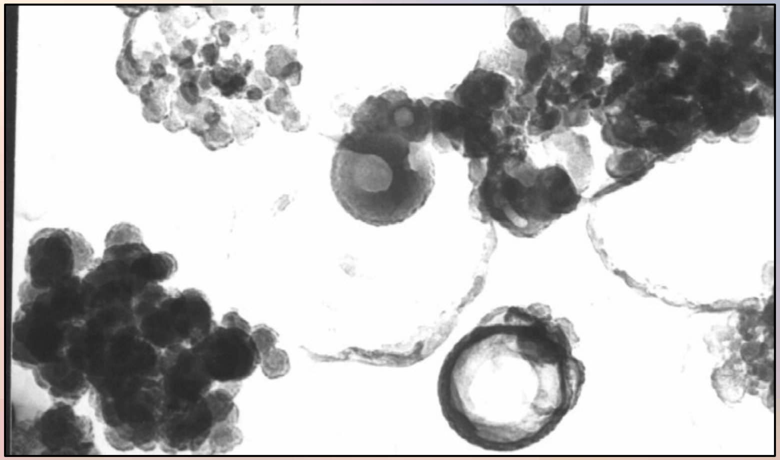


Fly ash



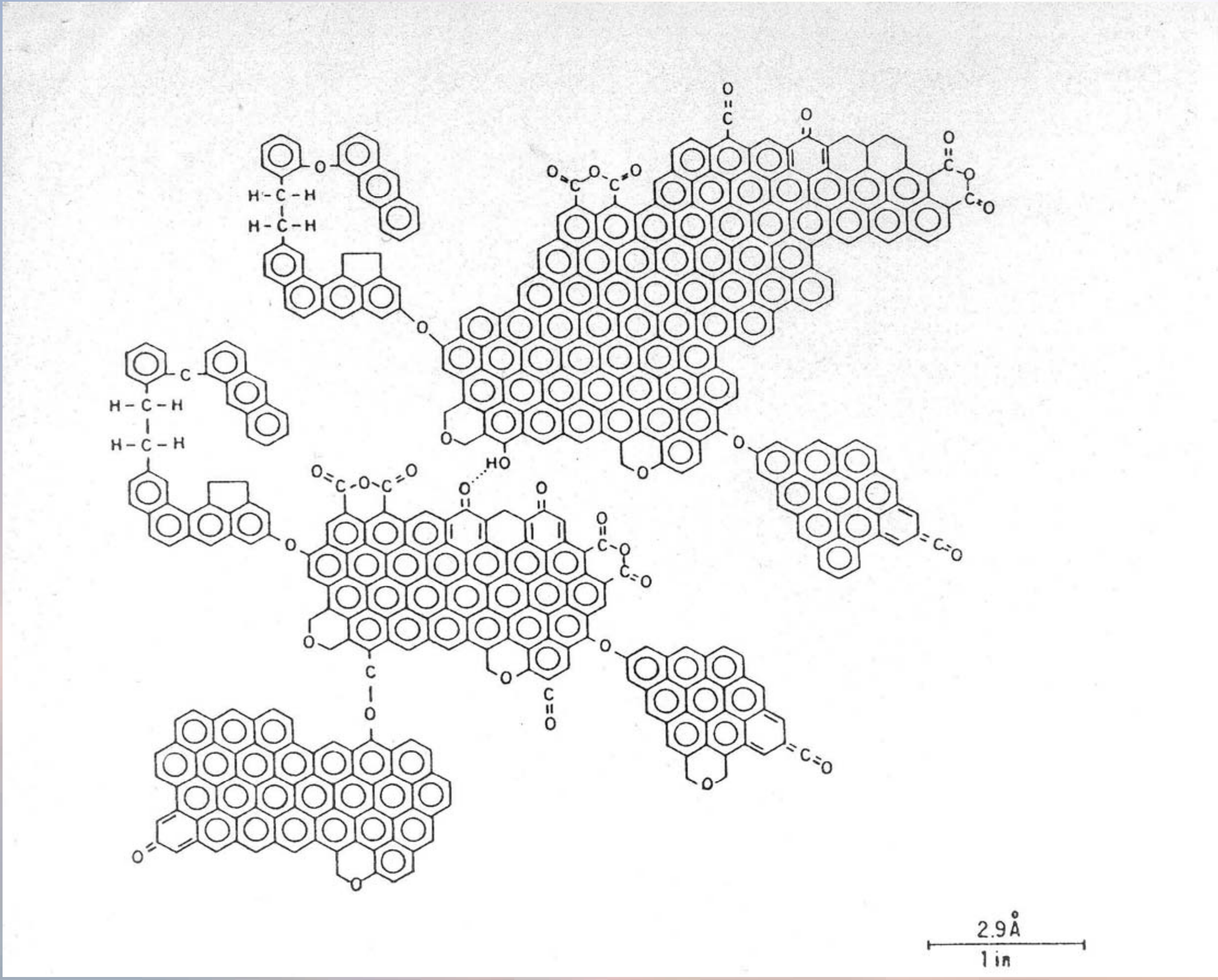
Courtesy of A. Lefevre

Biomass burning



Structure of Hexane Soot

(Akhter et al., 1985)



What are organic and elemental carbon?

Examples of Definitions

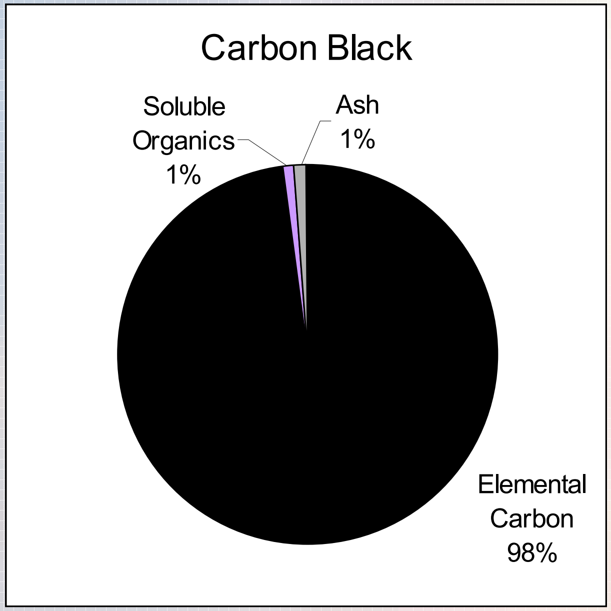
- Atmospheric EC is graphitic, but not graphite, diamond, or fullerene
- OC and EC are operationally defined by the measurement method, temperature protocol, and optical monitoring method
- EC is "a complex three-dimensional polymer with the capability of transferring electrons"

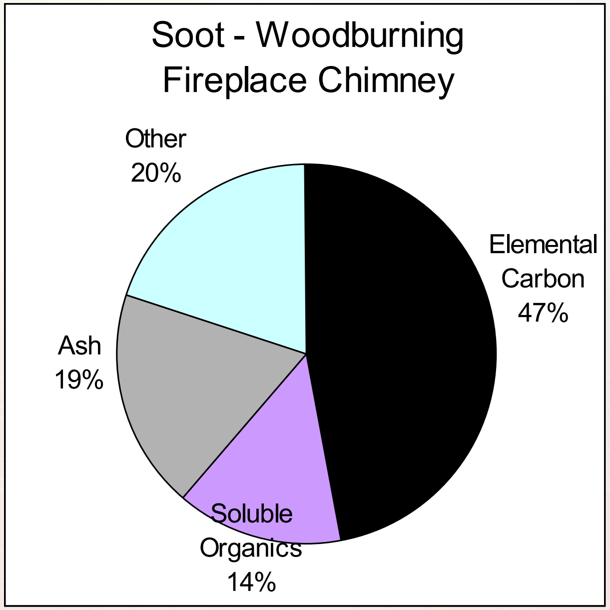
  (Chang et al. , 1982)
- EC is " 'soot' that forms when oxygen to carbon ratios during combustion are less than one"

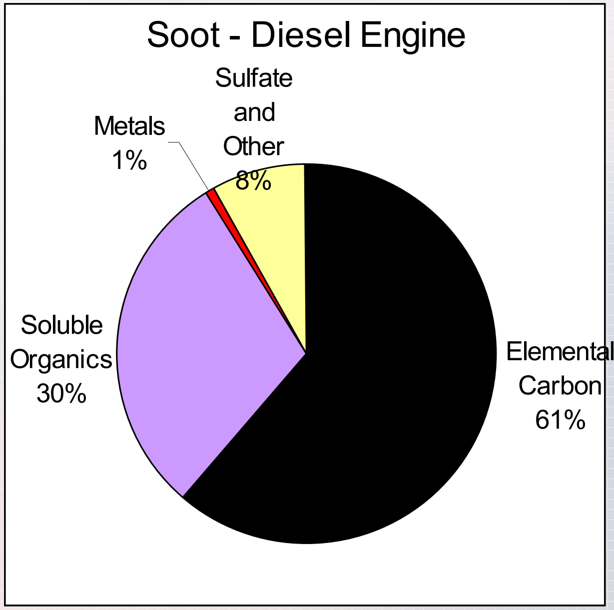
  (Seinfeld and Pandis, 1998)

Black carbon is not graphite
Carbon black is not soot

(Watson and Valberg, 2001)







Difficulties with OC and EC sampling and analysis

- No common definition of what "EC" is for atmospheric applications
- Light absorption efficiencies are not constant
  - They vary depending on particle shape and mixing with other substances
- OC and EC properties on a filter differ from those in the atmosphere
- OC gases are adsorbed onto the quartz filter at the same time that semi-volatile particles evaporate

Sampling

Quartz fiber filter:

- Positive artifact due to gas adsorption

  Correction: Parallel sampling with backup filter behind Teflon or quartz filter.

  Approach inadequate - variable adsorption characteristics.

- Negative artifact from evaporation of SVOC

Developing a measurement method

- In mid 1970's, particulate carbon measurements were deemed essential to determine the impact of emissions from automotive and other combustion sources to air quality.
- EC can only be derived from combustion sources while OC can have different origins
- TMO and GM two-step methods were used in the first Denver Brown Cloud Study (1980) – implicating automotive vehicles were major contributors to air pollution during winter in Denver
- Subsequent air quality and visibility studies routinely measure particulate carbon: SCENES, SCAQS (I,II,III), IMPROVE, etc.

At Least 15 International Thermal Combustion Carbon Methods

- Oregon Graduate Institute thermal optical reflectance (TOR) **(Huntzicker et al., 1982)**
- IMPROVE TOR and thermal optical transmittance (TOT) **(Chow et al., 1993, 2001)**
- NIOSH TOT **(NIOSH, 1999)**
- ACE-Asia TOT **(Mader et al., 2001)**
- Hong Kong University of Science and Technology UST-3 TOT **(Yang and Yu, 2002)**

At Least 15 International Thermal Combustion Carbon Methods (continued)

- Two-temperature thermal manganese dioxide oxidation (TMO) **(Fung, 1982,1990)**
- R&P two temperature **(Rupprecht et al., 1995)**
- French two-temperature pure oxygen combustion **(Cachier, 1989a, 1989b)**
- Lawrence Berkeley Laboratory continuous temperature ramp (EGA) **(Novakov, 1982)**
- German VDI extraction/combustion **(Verein Deutcher Ingenieure, 1999)**

At Least 15 International Thermal Combustion Carbon Methods (continued)

- Meteorological Service of Canada MSC1 TOT **(Sharma et al., 2002)**
- U.S. Speciation Trends Network (STN) TOT
- General Motors Research Laboratory two temperature **(Cadle et al., 1980)**
- Brookhaven National Laboratory two temperature **(Tanner et al., 1982)**
- Japanese two temperature **(Mizohata and Ito, 1985)**

Differences among Operating Parameters

- Combustion atmospheres
- Temperature ramping rates
- Temperature plateaus
- Residence time at each plateau
- Optical monitoring configuration and wavelength
- Standardization
- Oxidation and reduction catalysts
- Sample aliquot and size
- Evolved carbon detection method
- Carrier gas flow through or across the sample
- Location of the temperature monitor relative to the sample
- Oven Flush

Methods use one of two approaches:

1. Selective Oxidation Techniques

Examples:

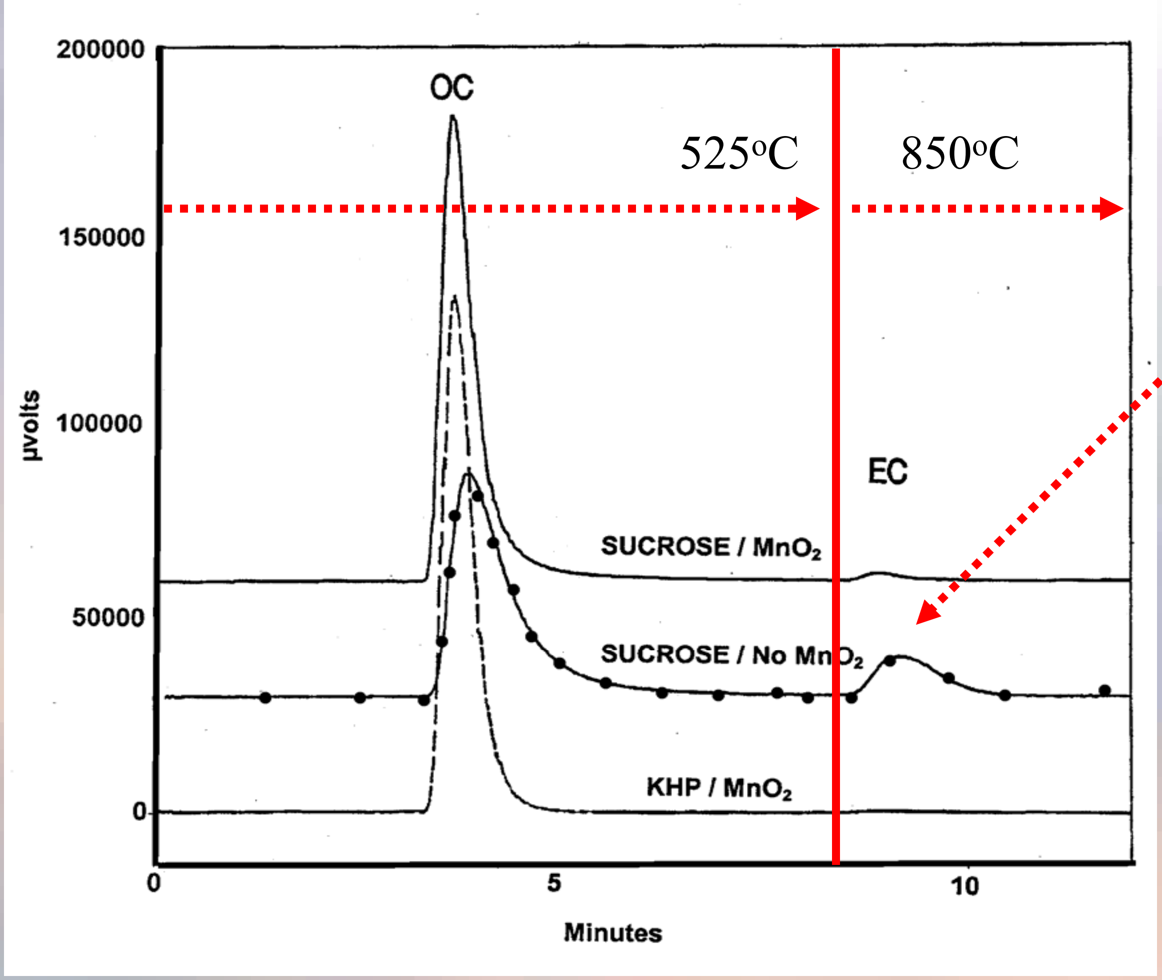
- **TMO** - MnO_2 at 525°C (Fung, 1982, 1990)
- **Evolved Gas Analysis** -100% O_2 , temp. ramping (Novakov, 1981)
- **2-step method** - 100% O_2 at 340°C - (Cachier, 1989)

Selective Thermal Oxidative Methods - Speciation Principles:

- Graphite (surrogate) is not oxidized by MnO_2 at 525^{o}C (TMO)
- EC is not oxidized by 100% O_2 at 340^{o}C (2-Step)
- Selected temperatures are upper limits of OC for each method.
- Pyrolysis is minimized - no correction is adopted
- Determine TOC and EC only, no other carbon fractions

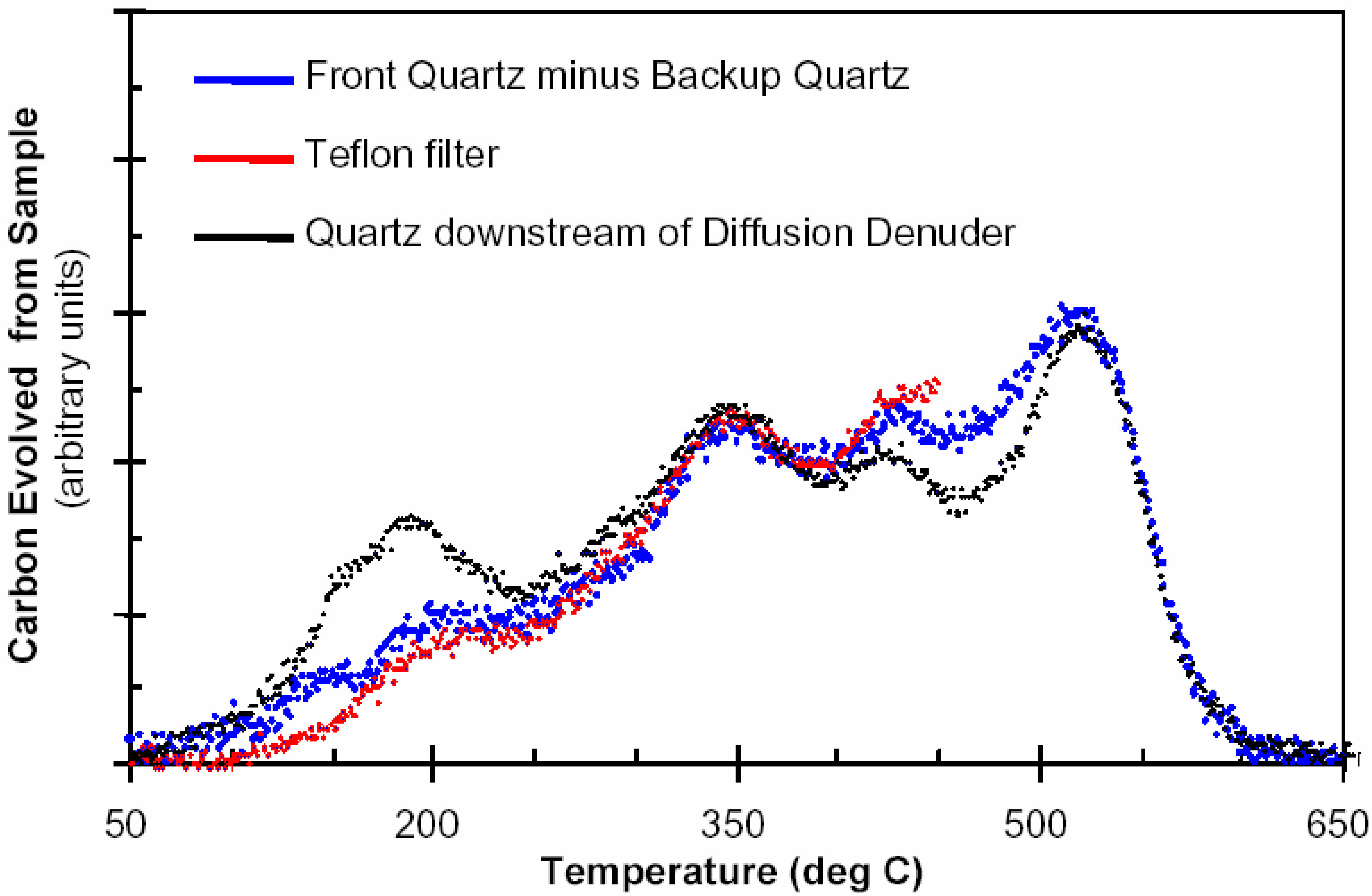
Availability of O_2 reduces pyrolysis

- Example: TMO analysis of sugar and KHP



EC from charring

Evolved Gas Analysis Thermogram



(Kirchstetter and Novokov, 2002, Presentation for DOE ACP)

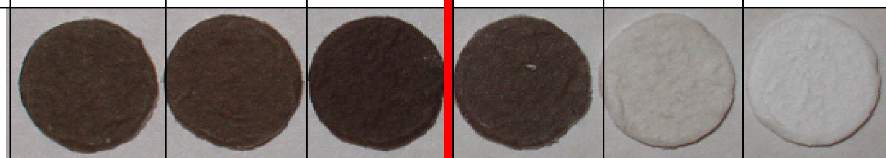
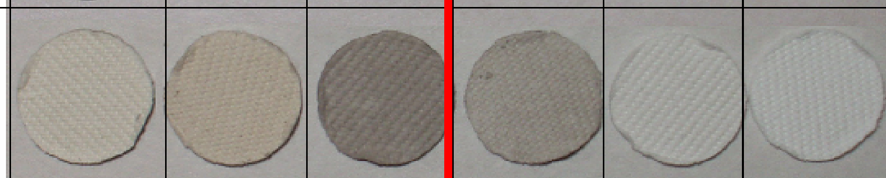
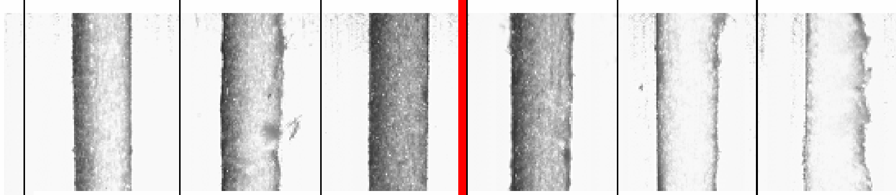
Second Approach: Thermo-volatilization in Helium

Speciation Principles

- EC is non-volatile; has strong light absorption and more resistant to oxidation than OC
- OC is volatile; has little light absorption comparing to EC
- Pyrolysis (charring) correction is used: by reflectance or transmittance.
- **Examples:** IMPROVE, NIOSH 5040 (variations - STN, MSC-1, etc.), GM two-step (no charring correction)

Why is pyrolysis correction necessary?

Sample 12/25/02 in IMPROVE Protocol

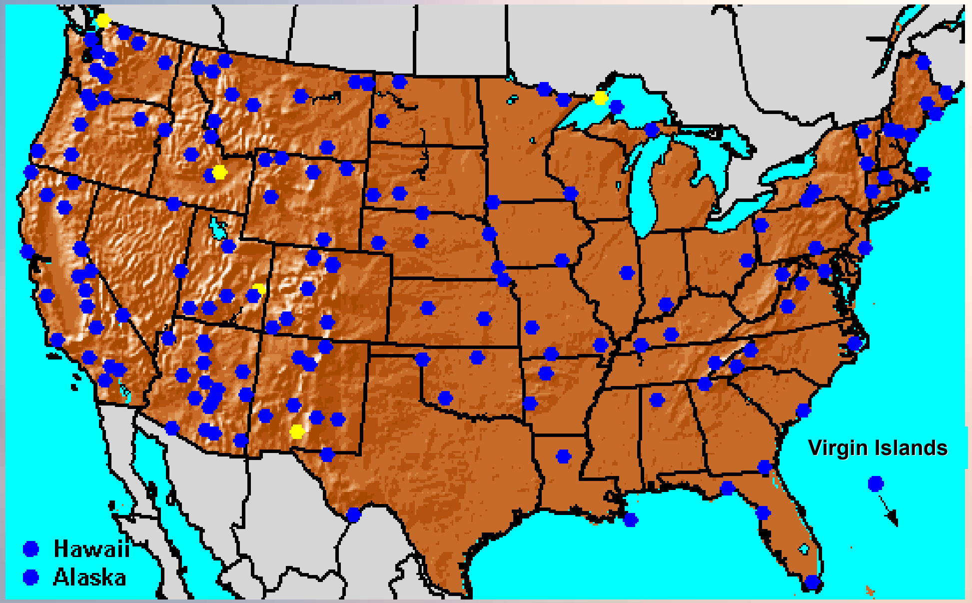
Temperature (°C) & Atmosphere	50 (He)	250 (He)	549 (He)	550 (He/O_2)	551 (He/O_2)	800 (He/O_2)
Reflectance (R)	588	582	516	575	1314	1561
Transmittance (T)	6	4	0	0	268	538
Front						
Back						
Cross Section Front ←→ Back						

Most used Methods: IMPROVE & NIOSH- Common Characteristics

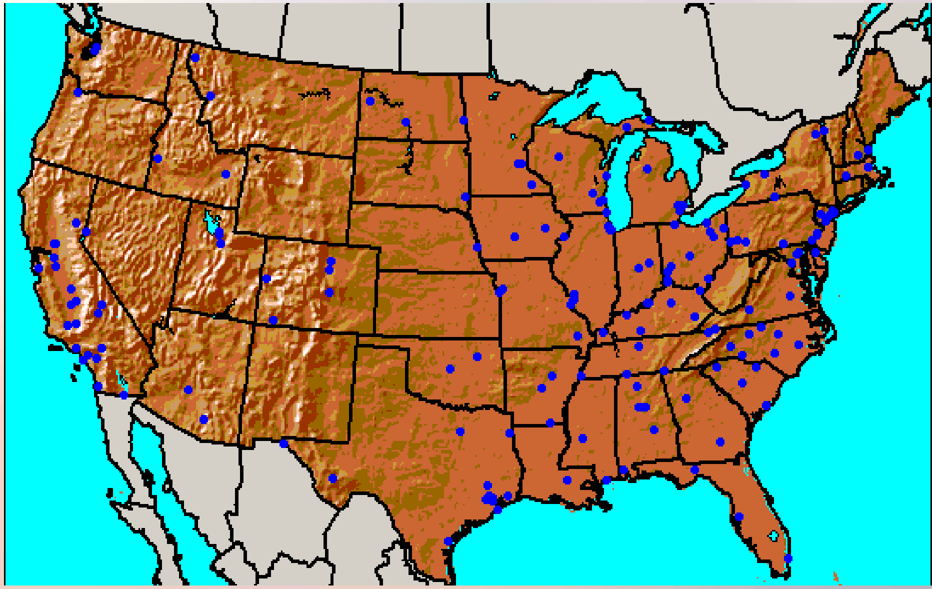
- OC is volatilized in helium
- Pyrolysis is monitored and corrected by laser reflectance (R) or transmission (T)
- EC is defined as carbon fraction oxidized after the laser signal returns to the initial level (optical charring correction)
- Have multiple temperature ramps

Non-Urban and Urban $PM_{2.5}$ Networks in U.S. Use Different Carbon Analysis Protocols that Give Different OC/EC Fractions

Non-Urban U.S. EPA **I**nteragency **M**onitoring of **PRO**tected **V**isual **E**nvironments (**IMPROVE**) Network



Urban U.S. EPA **S**peciation **T**rends **N**etwork (**STN**)



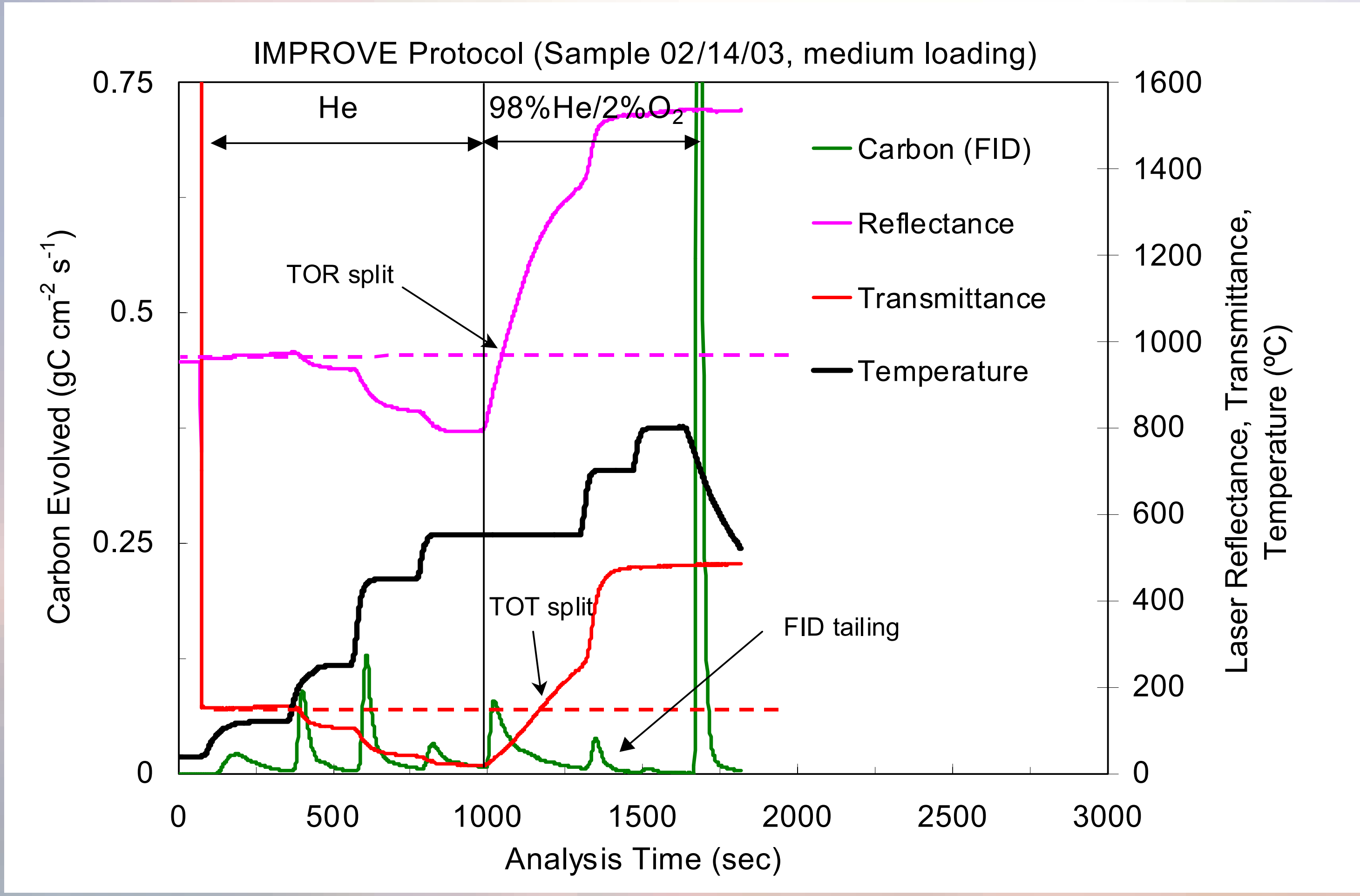
IMPROVE Method

Analytical Conditions:

- Thermal volatilization, with pyrolytic correction by laser reflectance (**R**)
- **4 OC fractions**: 120°, 250°, 450°, & 550°C in He (volatilization)
- **3 EC fractions**: 550°, 650°, & 800°C in 2%O_2/He (oxidation)
- **Residence time** at each temperature plateau: **varies** from 150 -580 sec.

IMPROVE

Corrects for pyrolysis by reflectance (TOR), has low initial temperatures (120 and 250˚C), long residence time (150-580 seconds) at each temperature, carbon peaks back to baseline, 550 ˚C max in He

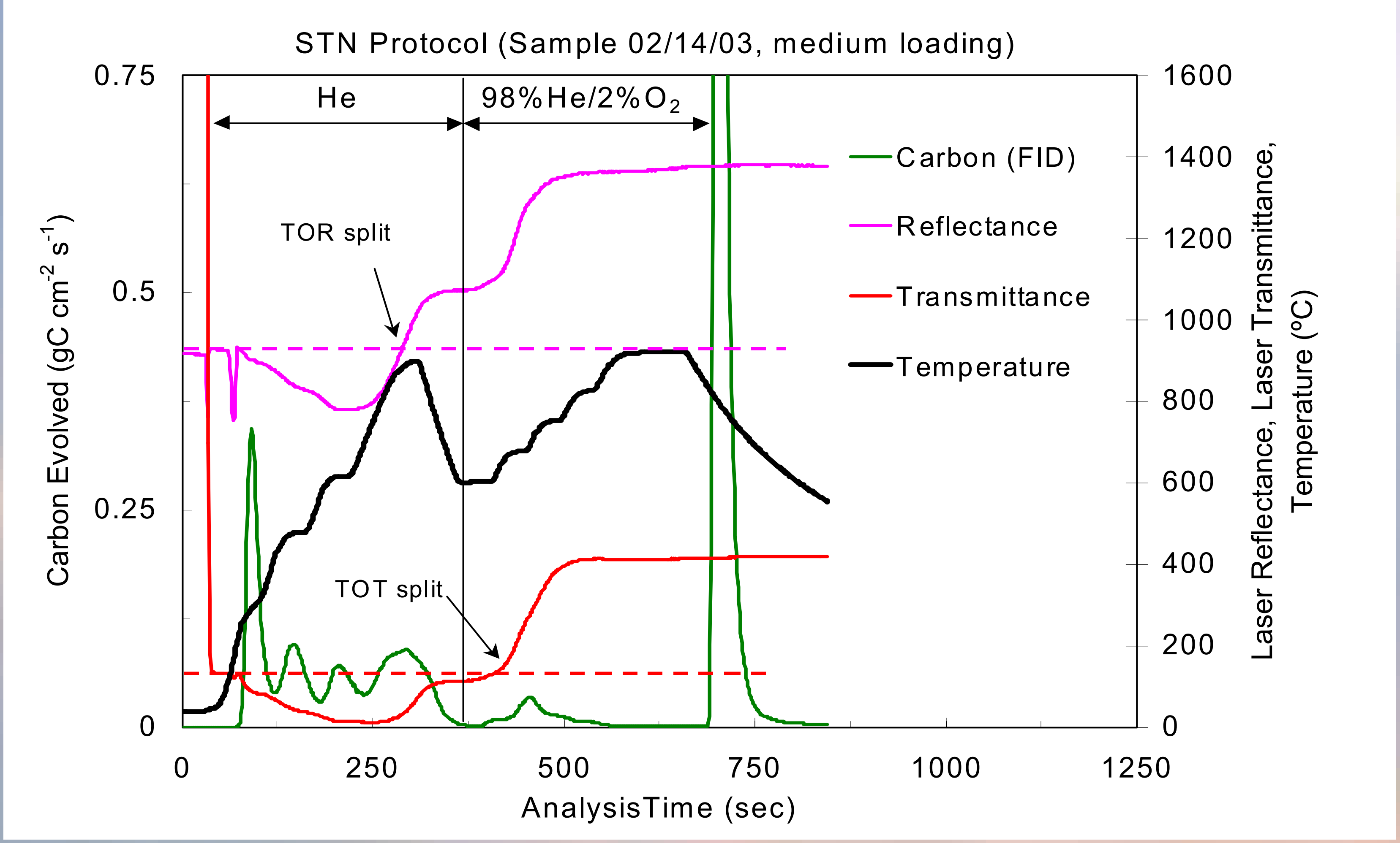


NIOSH Method

- Thermal volatilization, with pyrolytic correction by laser transmittance (T)
- 4 OC peaks: 250°, 400°, 550°, & 900°C in He (volatilization)
- 5 EC peaks: 600°, 675°, 750°, 825° & 920°C in 2%O_2/He (oxidation)
- NIOSH variants use different temperature ramps, but always have cooling between OC and EC transition

NIOSH/STN

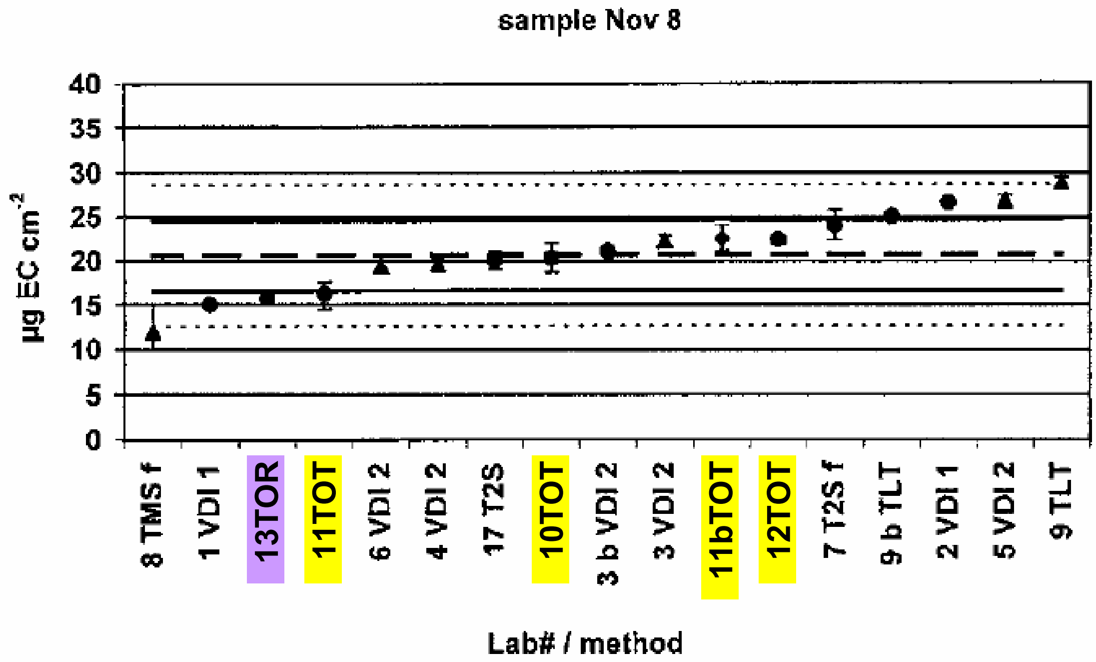
Corrects for pyrolysis by transmittance (TOT), has high initial temperature (310˚C), fixed and short residence times (45-120 seconds), 900 ˚C max in He

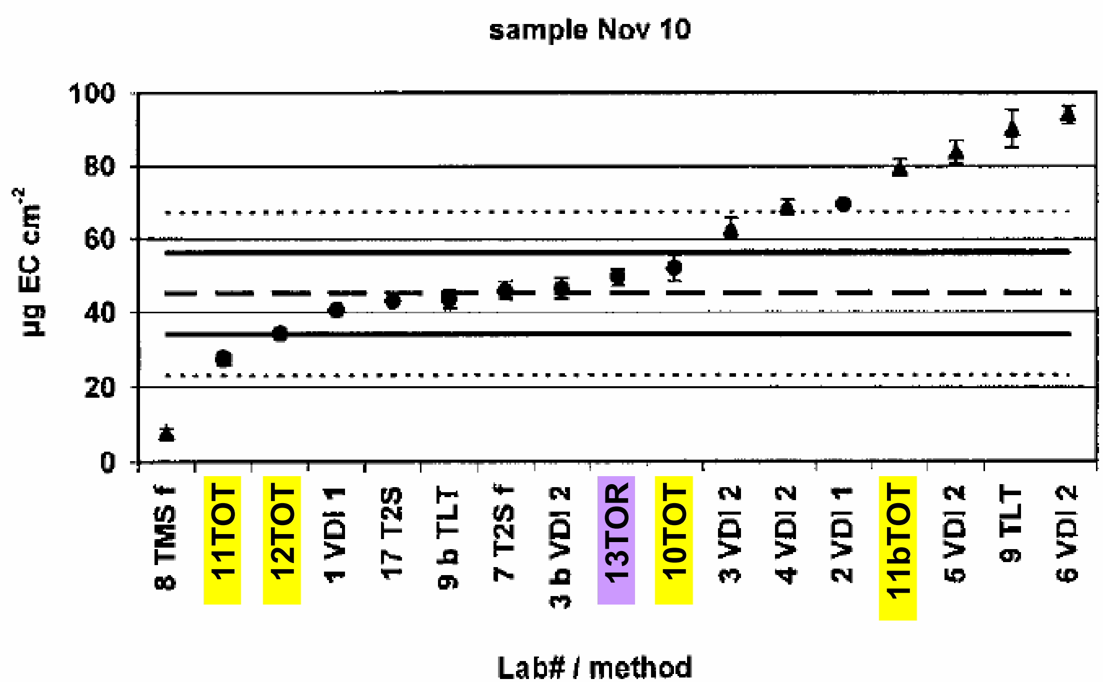


Different thermal evolution protocols give different results for black carbon

Schmid, H.P., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V.M.H., Bizjak, M., Burba, P., Cachier, H., Crow, D.J., Chow, J.C., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.P., Hitzenberger, R., et al., 2001. Results of the "Carbon Conference" international aerosol carbon round robin test: Stage 1. **Atmospheric Environment** 35 (12), 2111-2121.

Many called TOT, but temperature protocols differ from STN

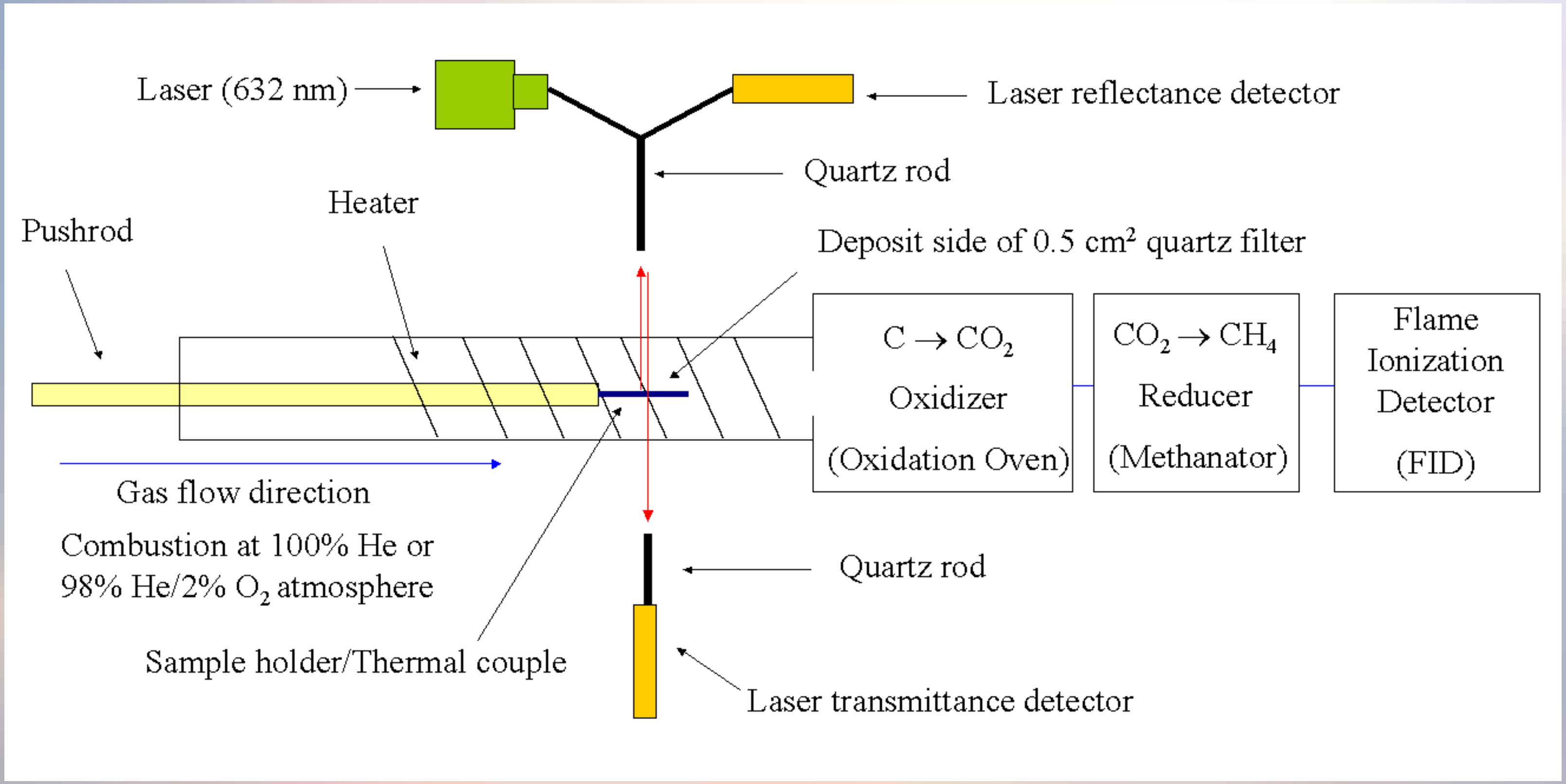




- Why do these methods yield different results?
- What are the contributing factors?
- We tried to answer these questions by studying IMPROVE and STN protocols because they are closely related and are most commonly used.

Evaluation Using a DRI Model 2001 Thermal/Optical Carbon Analyzer

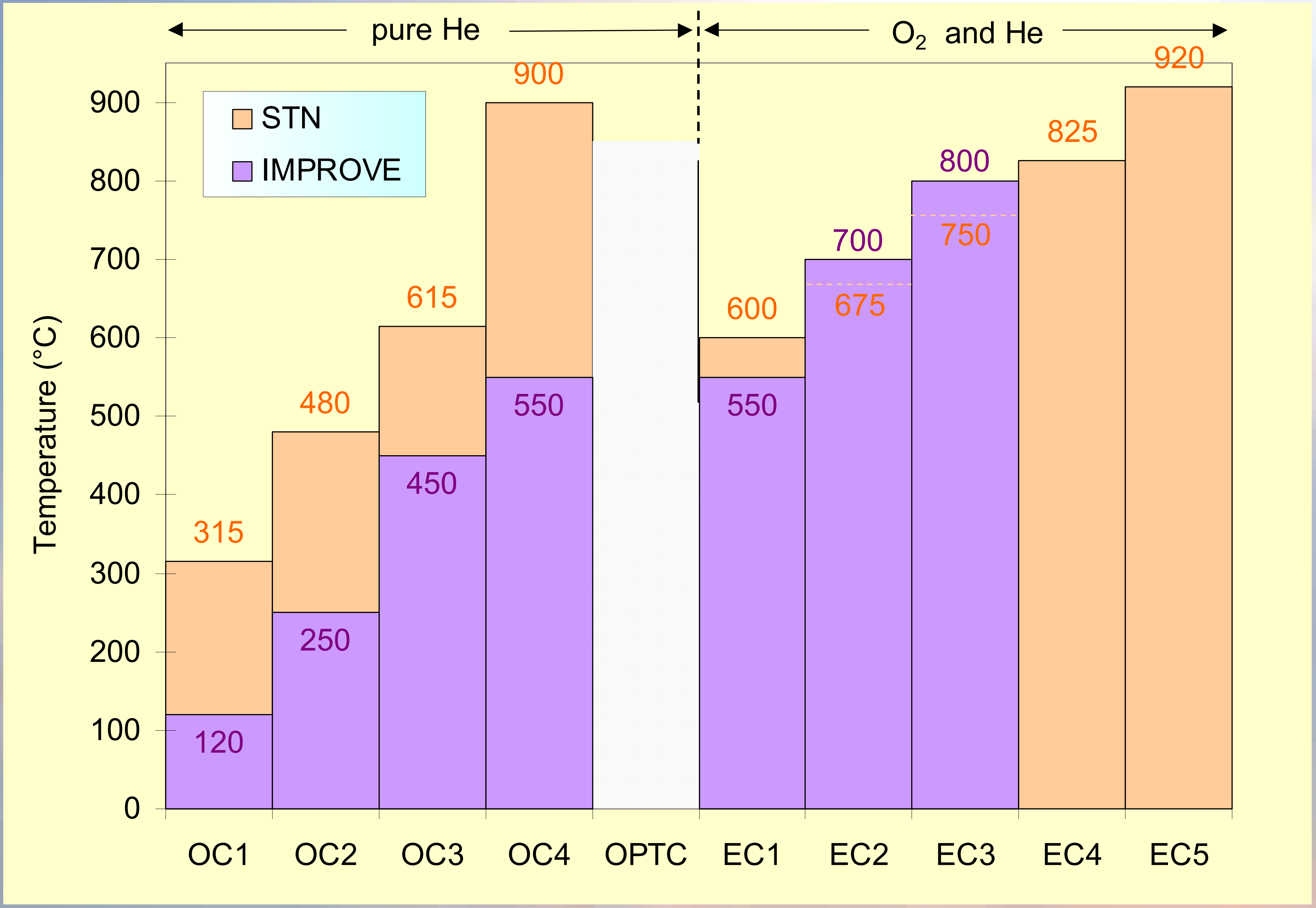
DRI Model 2001 with Simultaneous R & T monitoring Replicates the Conditions of Other Methods



DRI Model 2001 is a research tool as well as a production tool

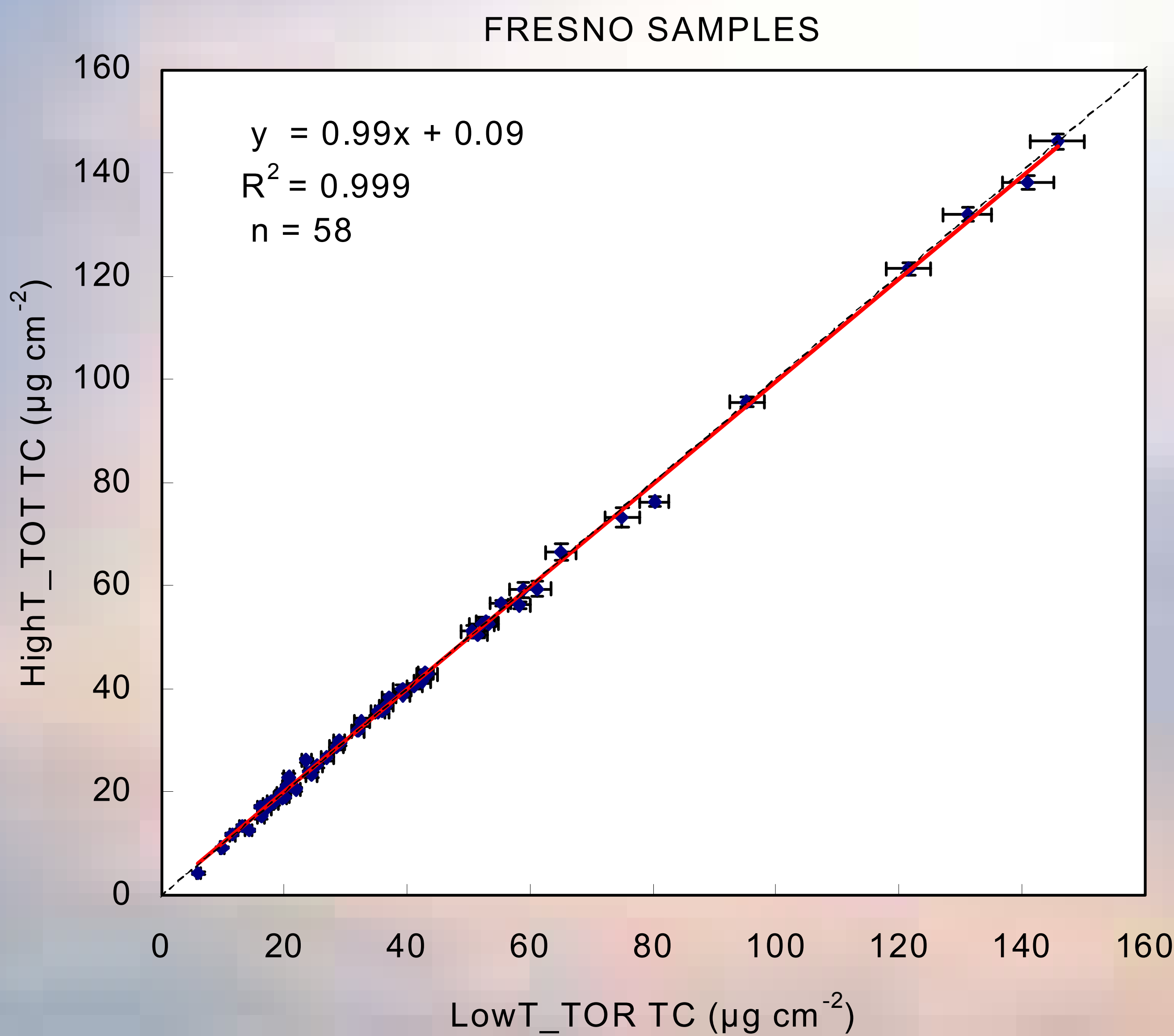
(Chow et al., 2004)

Comparison of IMPROVE/STN Temperature Profiles

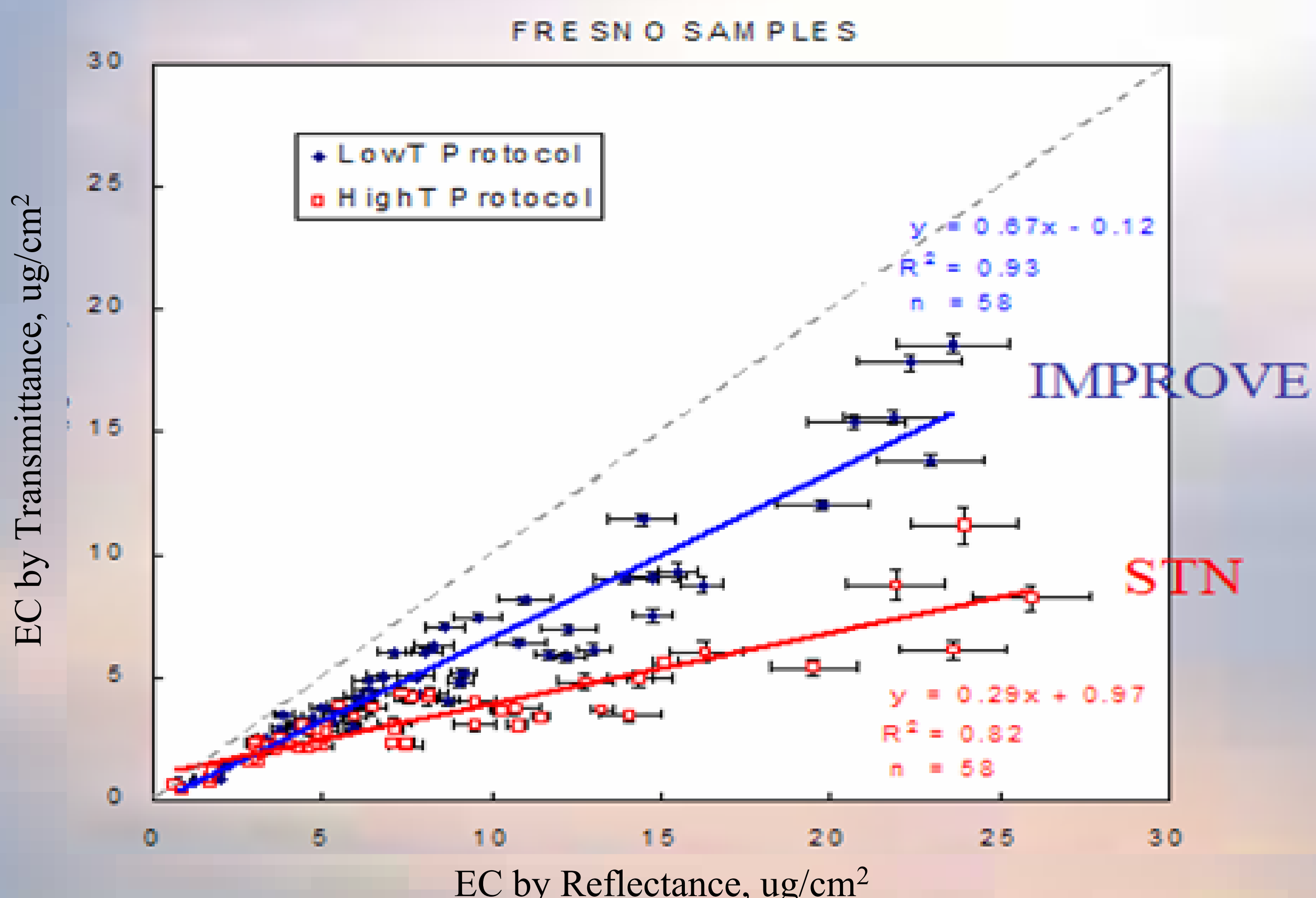


How do these two methods compare?

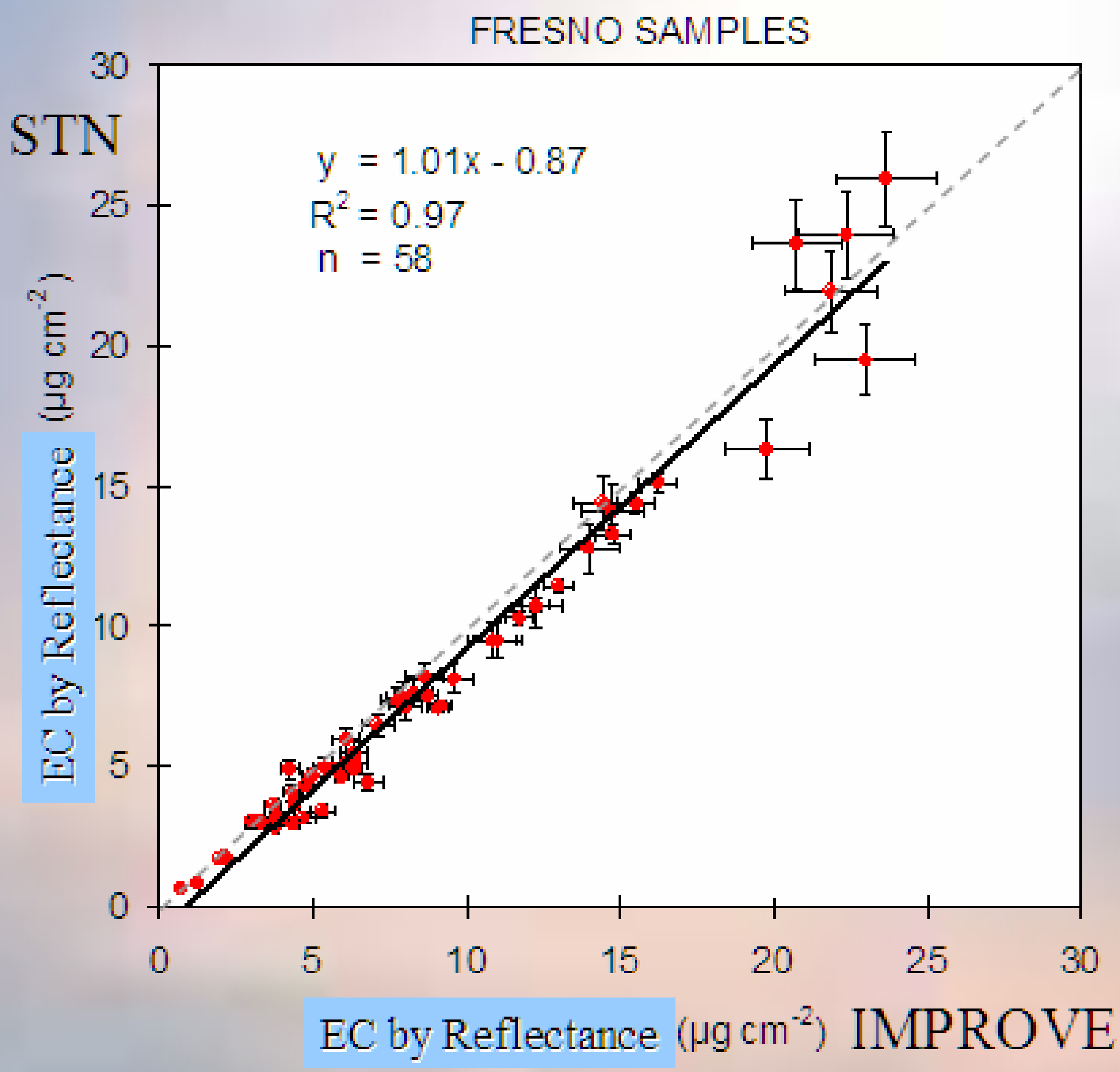
Total Carbon is the Same for IMPROVE and STN Protocols (Model 2001)



EC differs within protocol by reflectance (TOR) and transmittance (TOT) pyrolysis corrections



TOR Yields the Same EC for IMPROVE and STN Protocols Why?



Recent articles (*J. Aerosol Sci.*, *Environ. Sci. Technol.*) show TOR more robust than TOT methods

Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis

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Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols

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The sample affects the analysis

Factors affecting both methods

- Non-uniform filter deposit biases scaling from punch to whole filter
- Non-uniform filter punch deposit biases optical monitoring and charring
- Too light or too dark particle deposits make pyrolysis correction uncertain

Factors specific to each method:

- More heavily loaded samples require longer combustion time at each temperature step
- Minerals can oxidize EC at high temperatures in the He atmosphere
- Minerals can lower EC decomposition by catalytic reactions
- Optical properties of OC, EC, and minerals change with heating

STN versus IMPROVE – key areas of difference

- OC - STN 900^{o}C; IMPROVE 550^{o} C, in Helium

  (Causes matrix effects on EC)

- Pyrolysis correction: laser T (STN); R (IMPROVE)

  (Affects OC/EC split)

- Dwell time at each temperature plateau:

  STN- short, 90-120 sec.

  IMPROVE -Variable, 150 – 585 sec.

  (Affects observed carbon fractions)

To understand differences, test a few variables at a time, keeping everything else the same

Case 1: IMPROVE/STN temperatures

Case 2: TOT/TOR correction

Case 3: Residence time at temp. plateau

Case 1: Temperature/Matrix Effects

Using controlled samples containing

- Soot with iron oxide
- Iron oxide
- Soot only

UC-Davis : Ethylene / Acetylene / Fe(CO)5

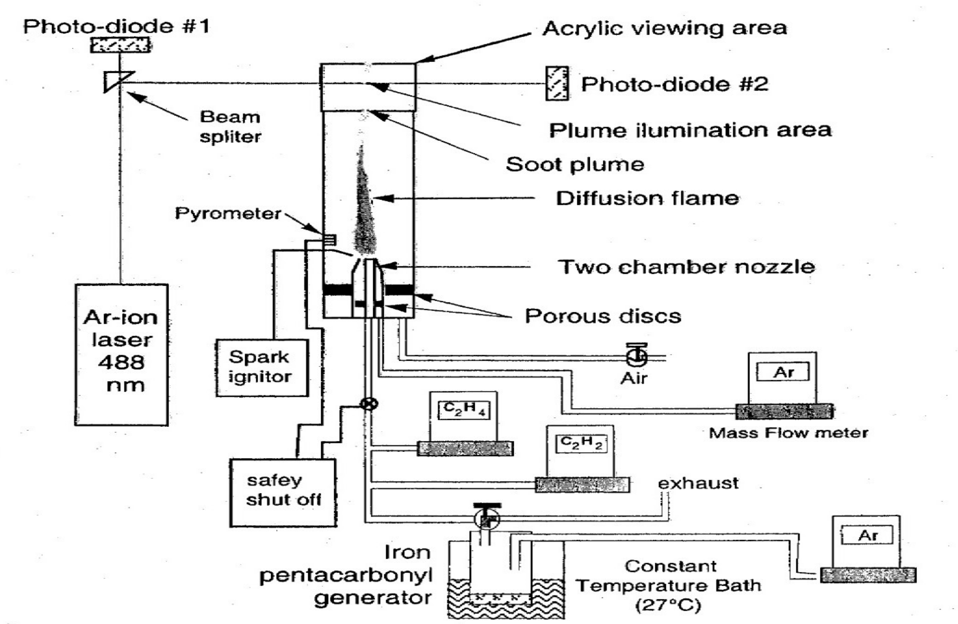
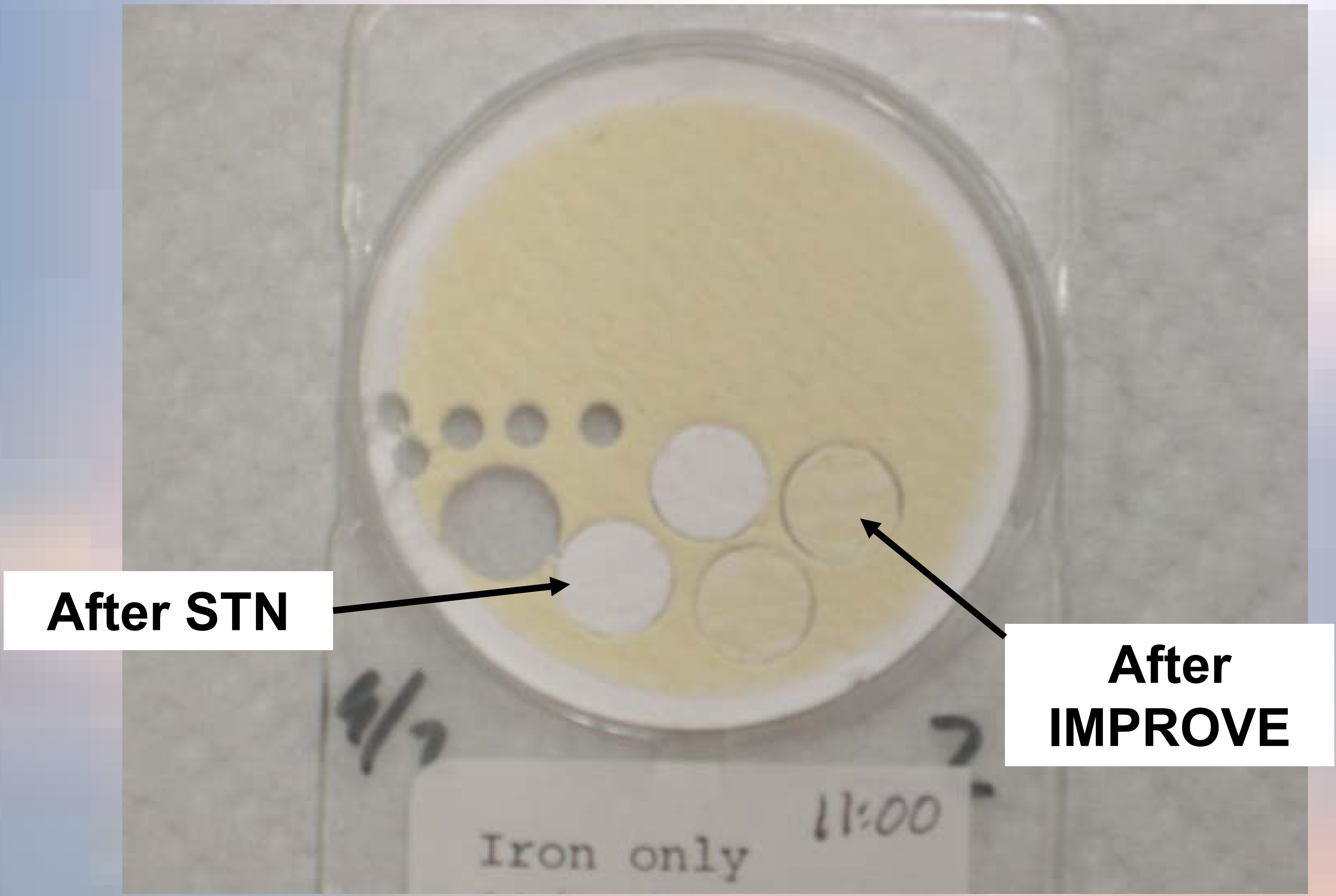


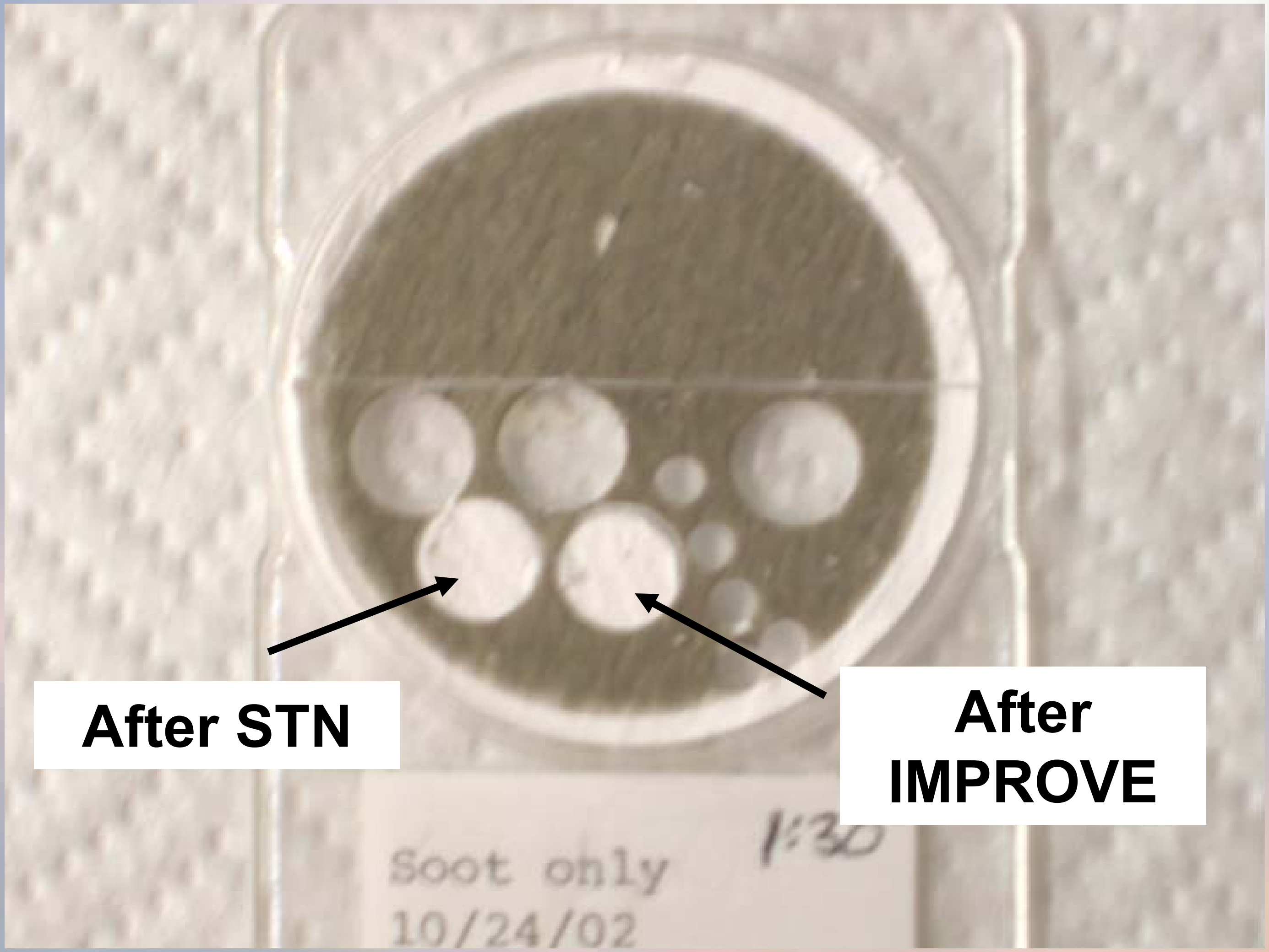
Figure 1. Diffusion flame apparatus.

Quartz filter, Fe oxides (~40nm)

No soot

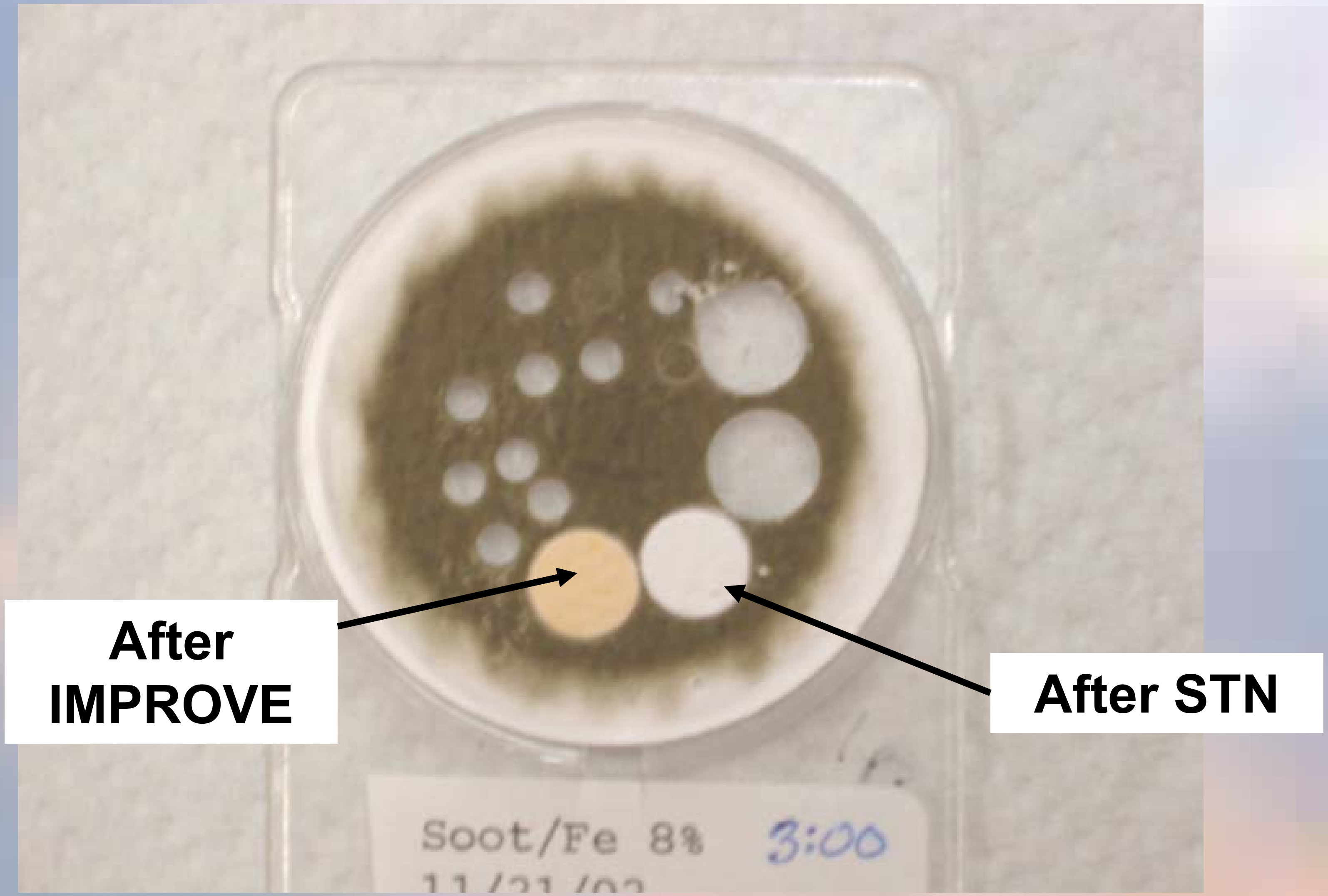


Soot only
No iron oxides



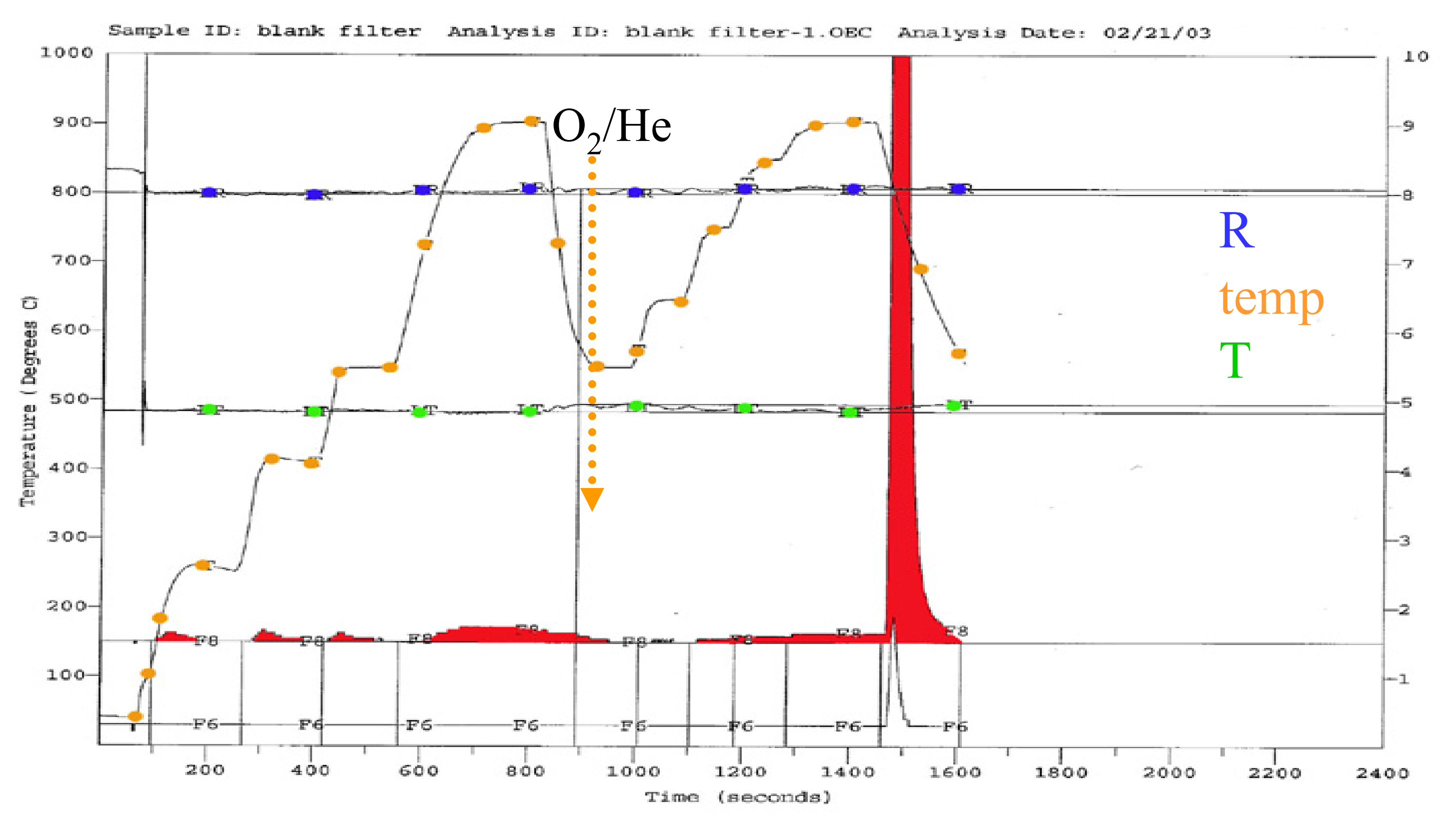
Soot with iron oxides

Ethylene + $Fe(CO)_5$ + Acetylene:



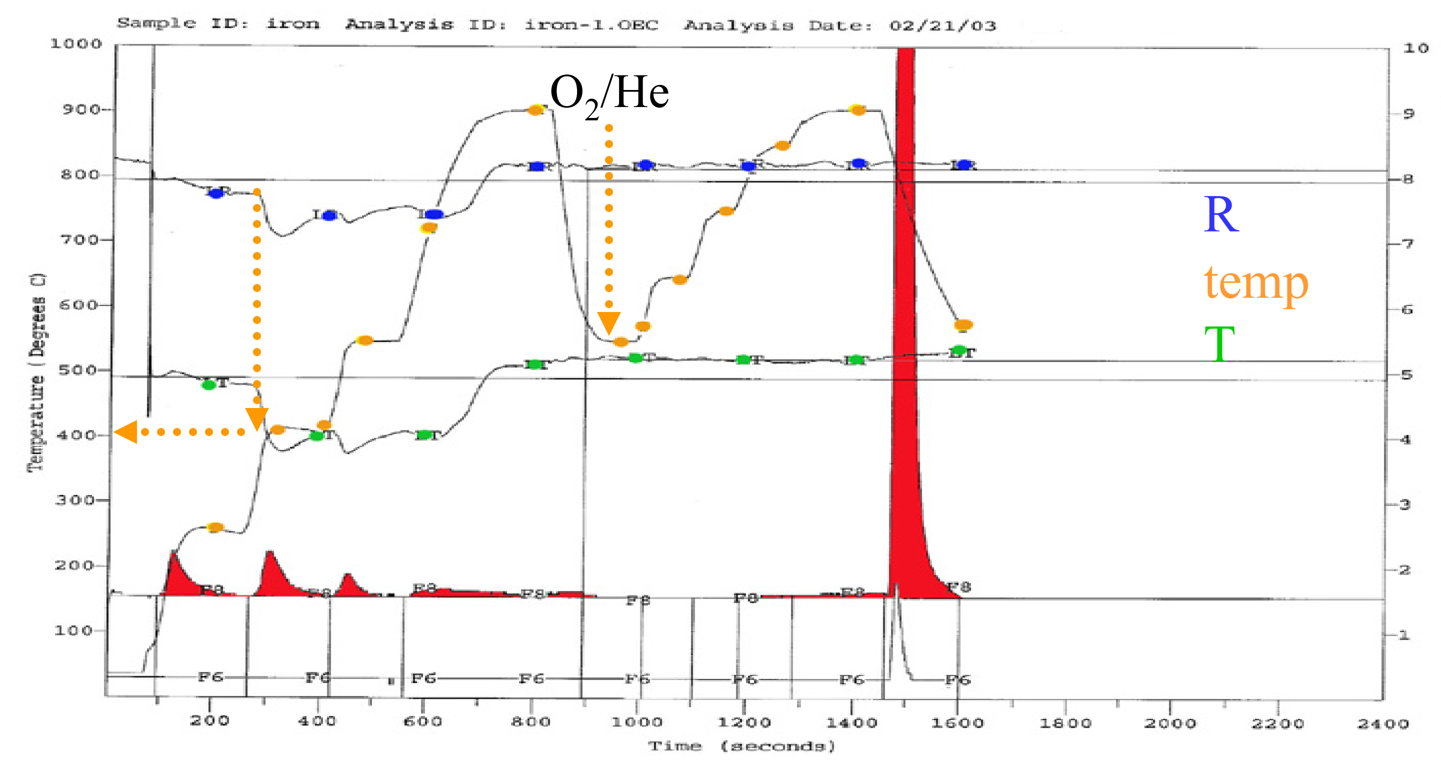
STN/NIOSH - Filter Blank

- Flat laser R and T:

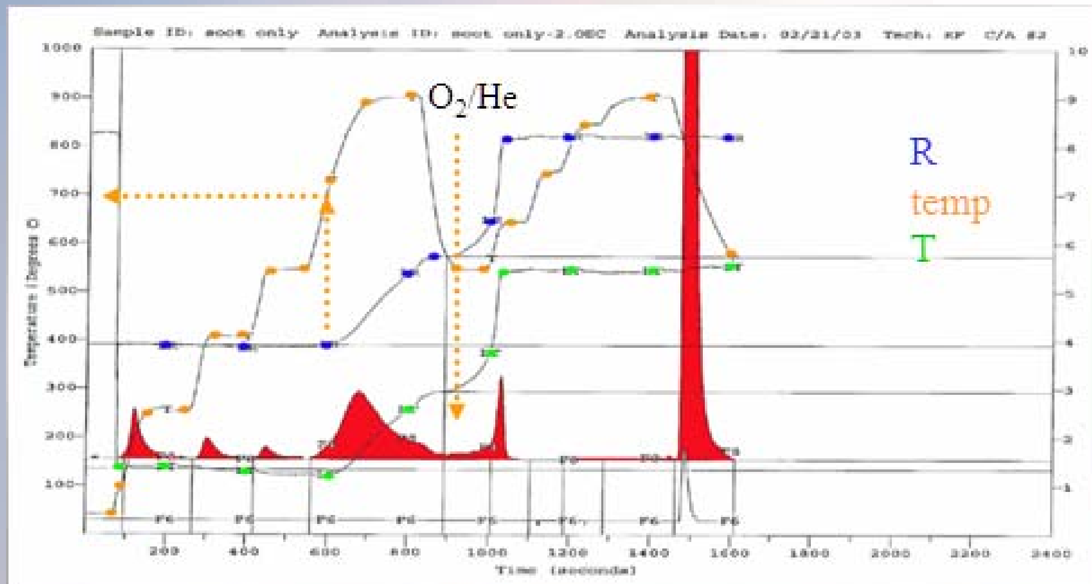


STN/NIOSH - Fe Oxides

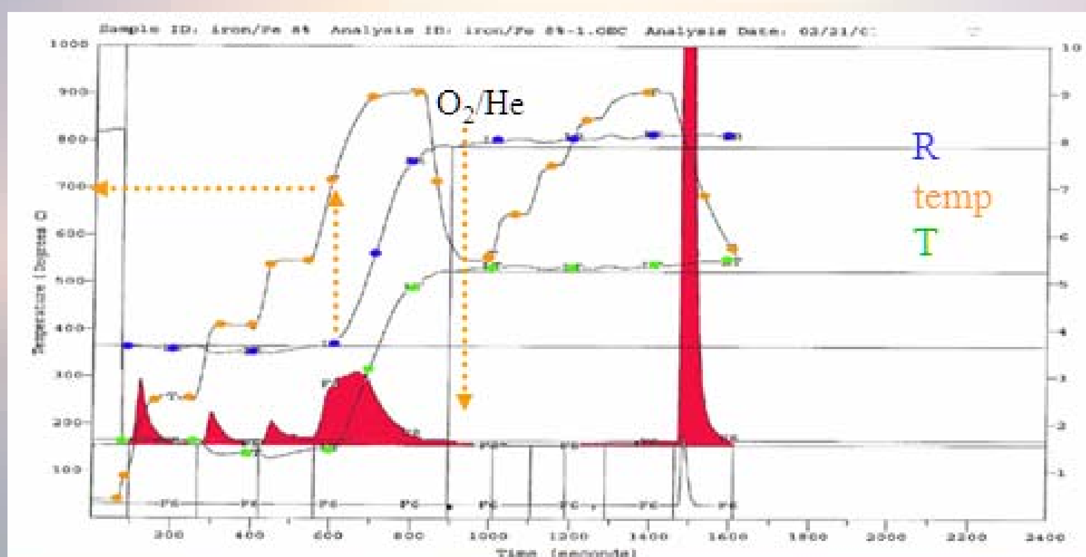
- Dipping of laser R and T at ~400^{o}C
- No residue after analysis



STN/NIOSH -



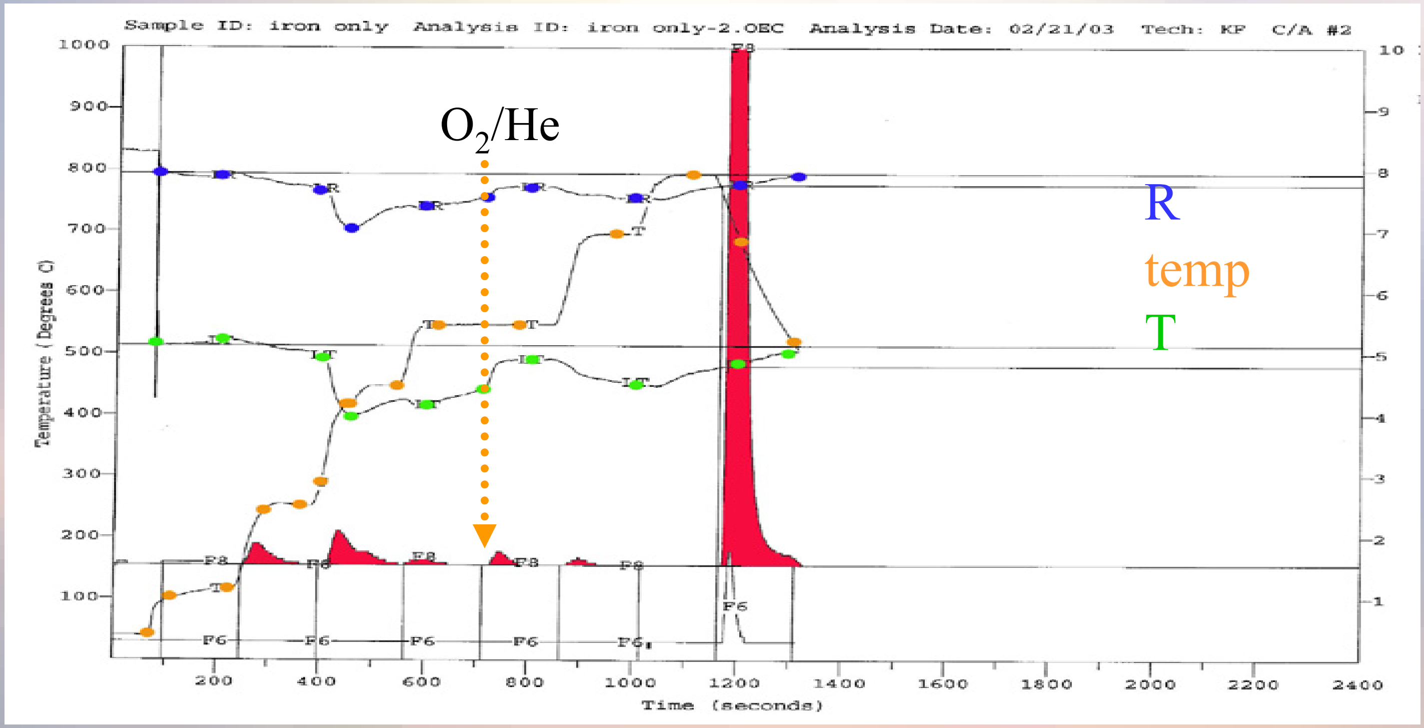
Soot only



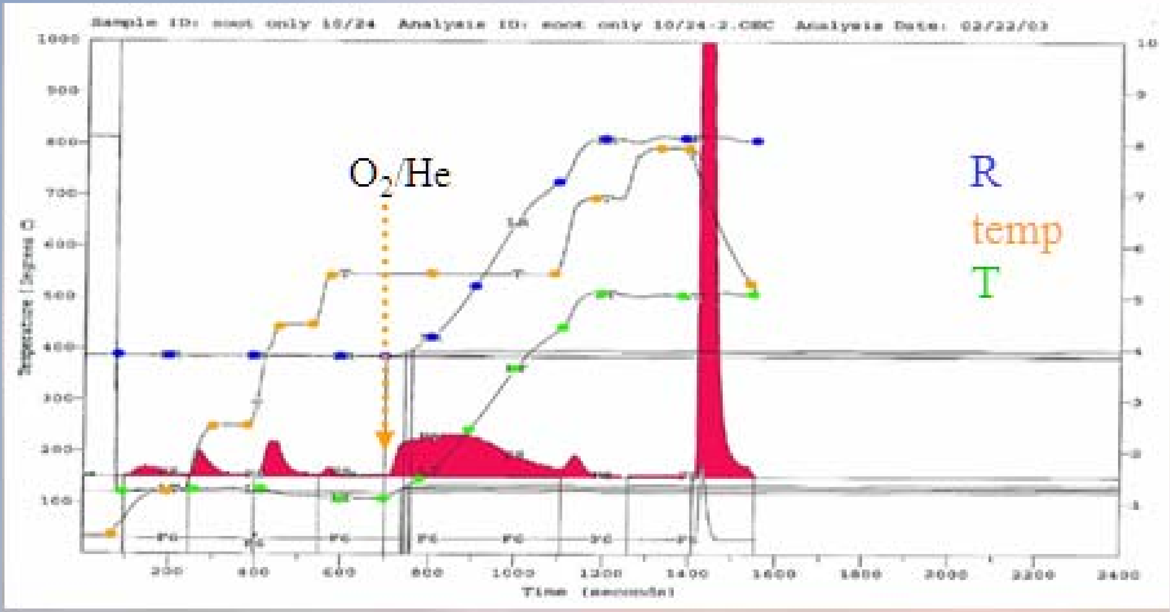
Soot with iron oxides

IMPROVE - Fe Oxides

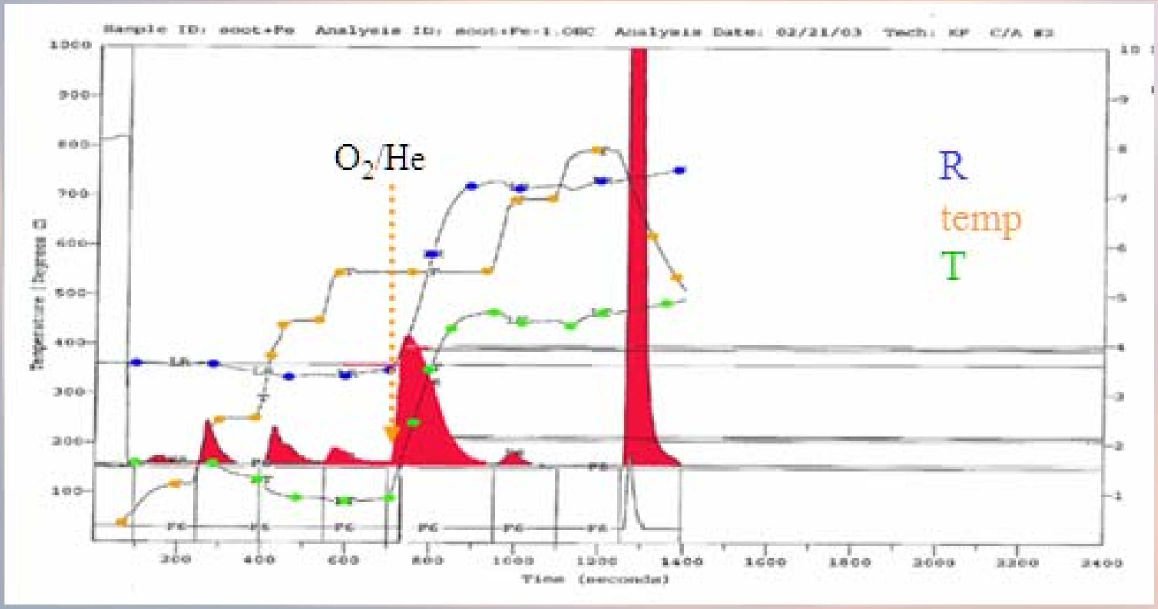
- Laser R and T dip & rise in He & O_2/He
- Orange residue after analysis



IMPROVE



Soot only



Soot with iron oxides

Temperature Effects -summary

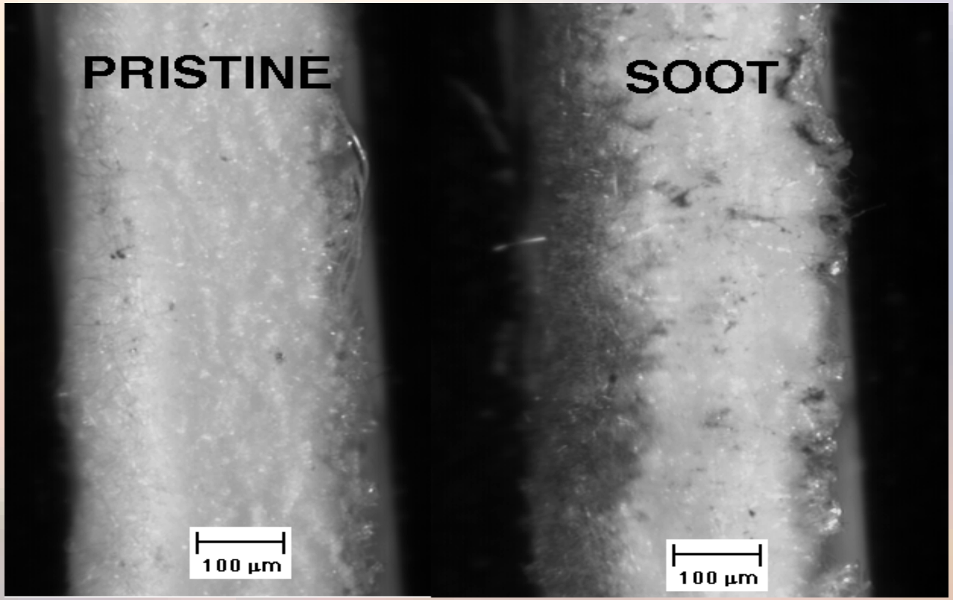
Mineral oxide particles:

- **May attenuate laser signal in both techniques.**
- **May interfere with pyrolysis correction - increase apparent OC.**
- **EC is oxidized by mineral oxides at 700-900 °C in He (as OC-4) in STN/NIOSH – "negative" pyrolytic carbon" (OP) for laser signal rising above initial before the introduction of O_2/He.**
- **Catalyze EC oxidation at 550°C in O_2/He in IMPROVE - No effect on EC results.**
- **Laser T is solely used for OC/EC split in STN regardless of sample atmosphere (He or O_2/He).**

Case 2: Laser T vs R - Effect on results

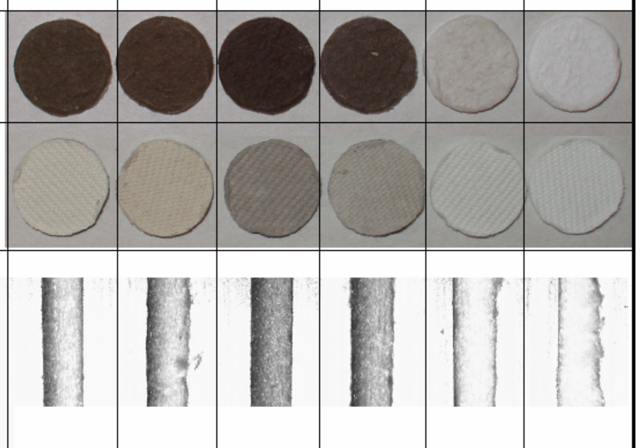
- R sees charring changes on filter surface
- T sees changes on and within filter
- Charring within is temperature dependent

➢ NIOSH - Pyrolysis correction is larger – resulting in higher OC, and lower EC

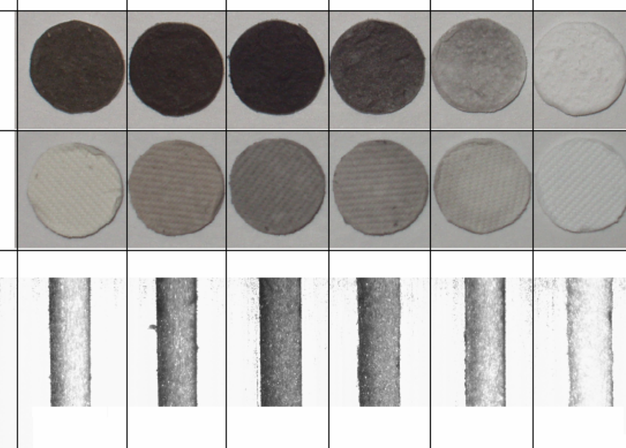


Within filter charring is larger for STN because initial temperature steps are higher: less OC to char with IMPROVE and correction is smaller

Sample 12/25/02 in IMPROVE Protocol

Temperature (°C) & Atmosphere	50 (He)	250 (He)	549 (He)	550 (He/O_2)	551 (He/O_2)	800 (He/O_2)
Reflectance (R)	588	582	516	575	1314	1561
Transmittance (T)	6	4	0	0	268	538
Front						
Back						
Cross Section Front ←→ Back						

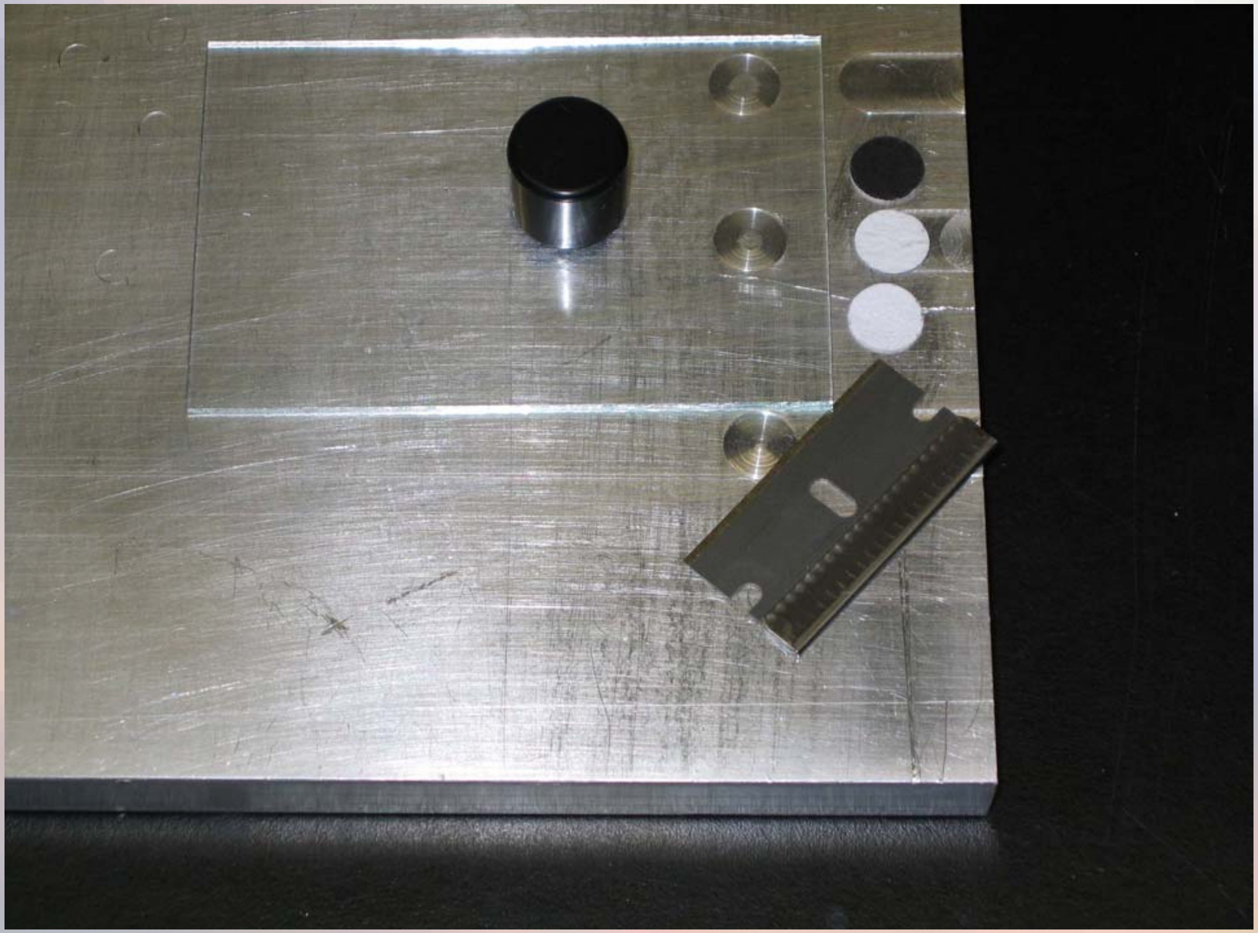
Sample 12/25/02 in STN Protocol

Temperature (°C) & Atmosphere	50 (He)	609 (He)	897 (He)	644 (He/O_2)	677 (He/O_2)	920 (He/O_2)
Reflectance (R)	587	507	365	573	897	1564
Transmittance (T)	5	0	0	0	4	534
Front						
Back						
Cross Section Front ←→ Back						

TOR is less sensitive to internal charring than TOT because it is dominated by the surface deposit, not by charred organic vapors in the filter

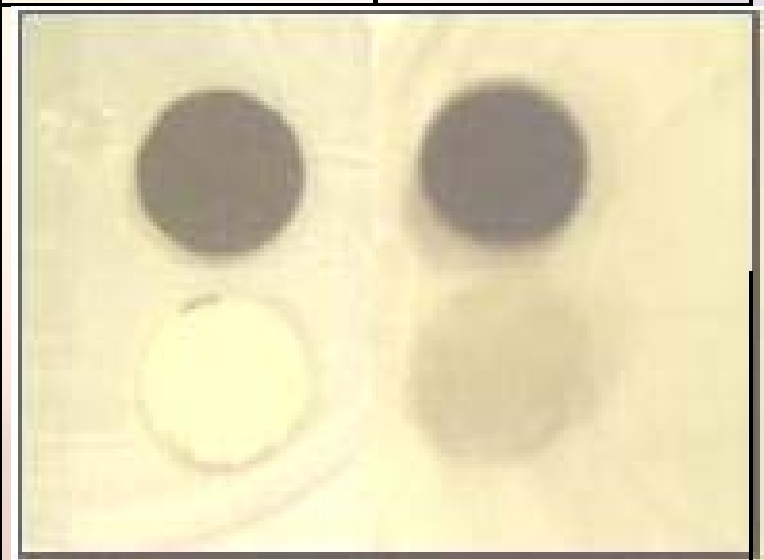
Is internal charring due to particles?

We sliced the filter, only the top half with particles

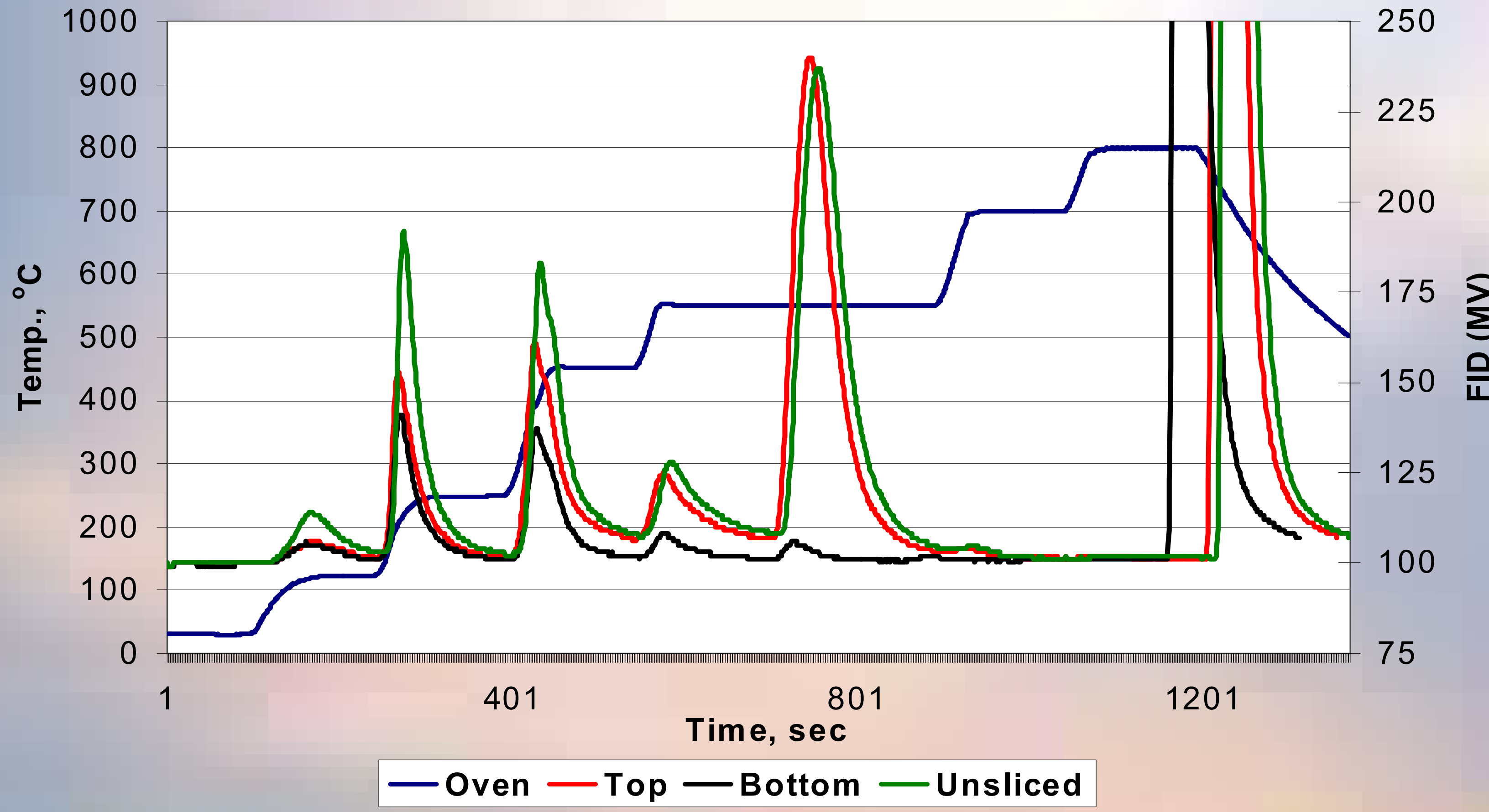


Adsorbed organic vapor within the filter char

	Initial	Max. Char
Top Half		
Bottom Half		



Carbon in top and bottom half of filter
Much of low temperature OC is adsorbed organic vapor



Recent article identified artifact compounds

ELSEVIER
Atmospheric Environment 39 (2005) 6945–6956
www.elsevier.com/locate/atmosenv

Sampling artifact estimates for alkanes, hopanes, and aliphatic carboxylic acids

Tanasri Sihabut[a], Joshua Ray[a,1], Amanda Northcross[a,2], Stephen R. McDow[b,*]

[a]Environmental Science Program, Drexel University, Philadelphia, PA, USA
[b]Human Exposure and Atmospheric Sciences Division, US Environmental Protection Agency, Research Triangle Park, NC 27711, USA

Received 3 September 2004; accepted 28 February 2005

Northeast Oxidant and Particulate Study:
Artifact compounds from hi-vol backup quartz filter

- n-alkanes C23-C28
- hopanes C27-C30
- n-carboxylic acids C15-C18
- dicarboxylic acids C3-C9

Case 2: Summary

- TOR is less sensitive to internal charring than TOT because it is dominated by the surface deposit, not by charred organic vapors in the filter
- EC determined by TOR approach is not sensitive to the temperature protocol used
- Internal charring is sensitive to temperature applied
- TOT charring correction is larger due to inclusion of internal charring, leading to lower EC than TOR

Case 3: Dwell time at temperature plateaus

- IMPROVE's dwell time is peak slope driven, increasing dwell time for larger peaks. So evolved peaks are well resolved
- STN's dwell time is fixed regardless of peak size. The tail portion of a large peak may become part of the next temperature fraction.
- Hence dwell time affects the agreements in OC fractions between IMPROVE and STN

Summary - factors contributing to the difference between STN and IMPROVE

- **Temperature:**
  - Higher temperatures enhance matrix effects such as oxidation & catalytic reactions
  - Charring is more likely at higher temperatures
  - Temperatures specified by thermal protocols may not be the actual sample temperatures
  - This temperature bias causes variations in carbon fractions and contribute to discrepancies in interlab comparisons and uncertainties in receptor modeling using carbon fractions.

Summary - continued

- **Residence time**:
  - Shorter time at a given temperature leads to less resolved OC fractions, causing more OC to evolve at the next step
  - Shifting more OC towards higher temperature could result in higher charring propensity
- **Pyrolysis Correction**:
  - Transmittance is influenced by internal charring, leading to a greater correction.
  - Reflectance is affected mainly by the particulate deposit, so a smaller correction.

Conclusions about TOR vs TOT

- EC by IMPROVE and STN are the same by TOR for pyrolysis correction of the surface deposit, but different for TOT with pyrolysis throughout the filter
- Pyrolysis takes place throughout the filter owing to adsorbed organic vapors during sampling, adsorbed vaporized particles during analysis, or liquid organic particles
- Higher initial STN temperatures result in more pyrolysis on and within the filter than the lower IMPROVE temperatures. Less OC is available for pyrolysis with IMPROVE

Conclusions – cont.

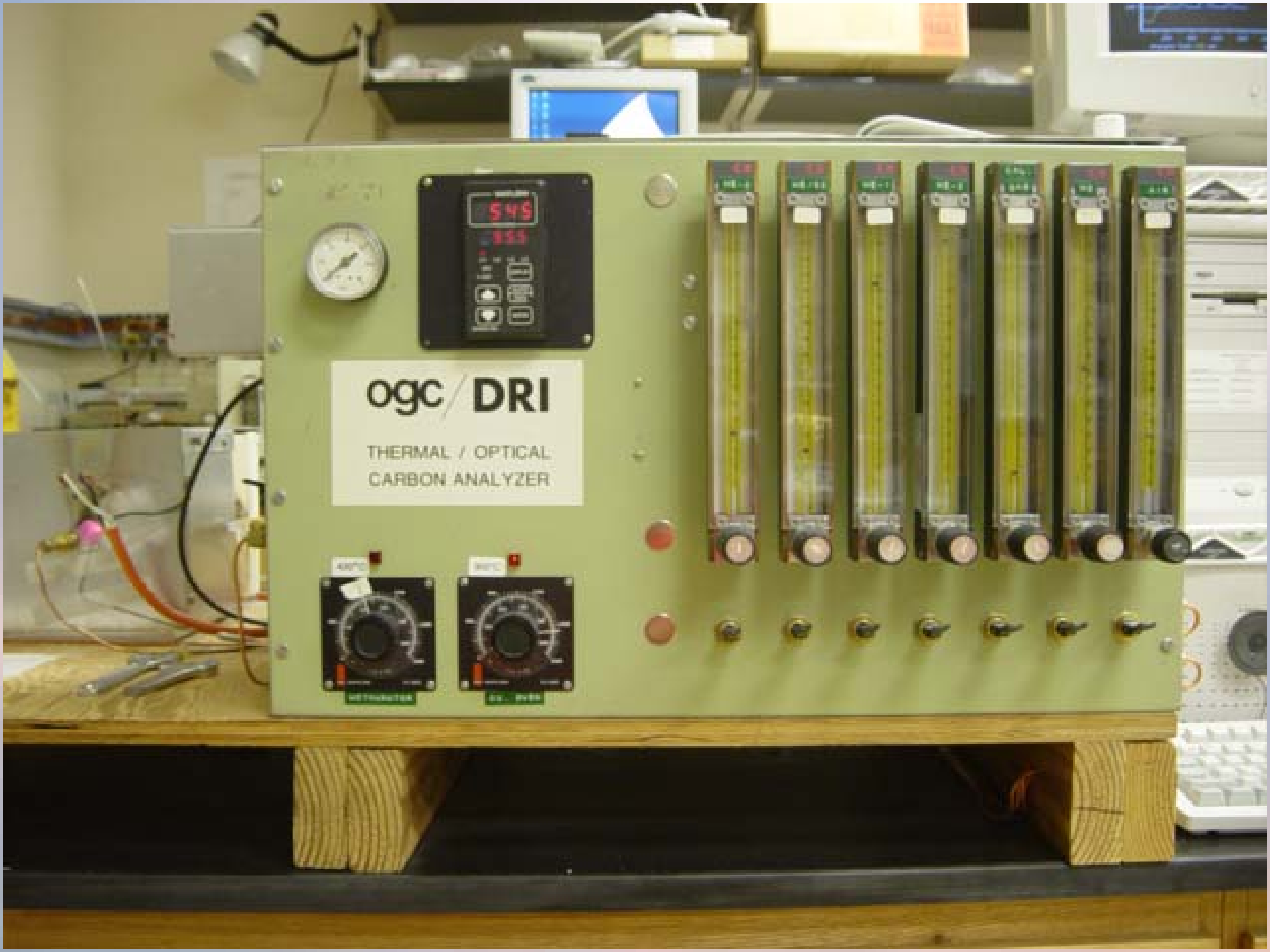
- Higher temperatures enhance EC oxidation when other materials are present
- Decomposition of colored minerals changes reflectance and transmittance, biasing TOR and TOT corrections
- STN Network is switching to the IMPROVE protocol to be consistent with the IMPROVE Network

Potential Differences from Analyzers

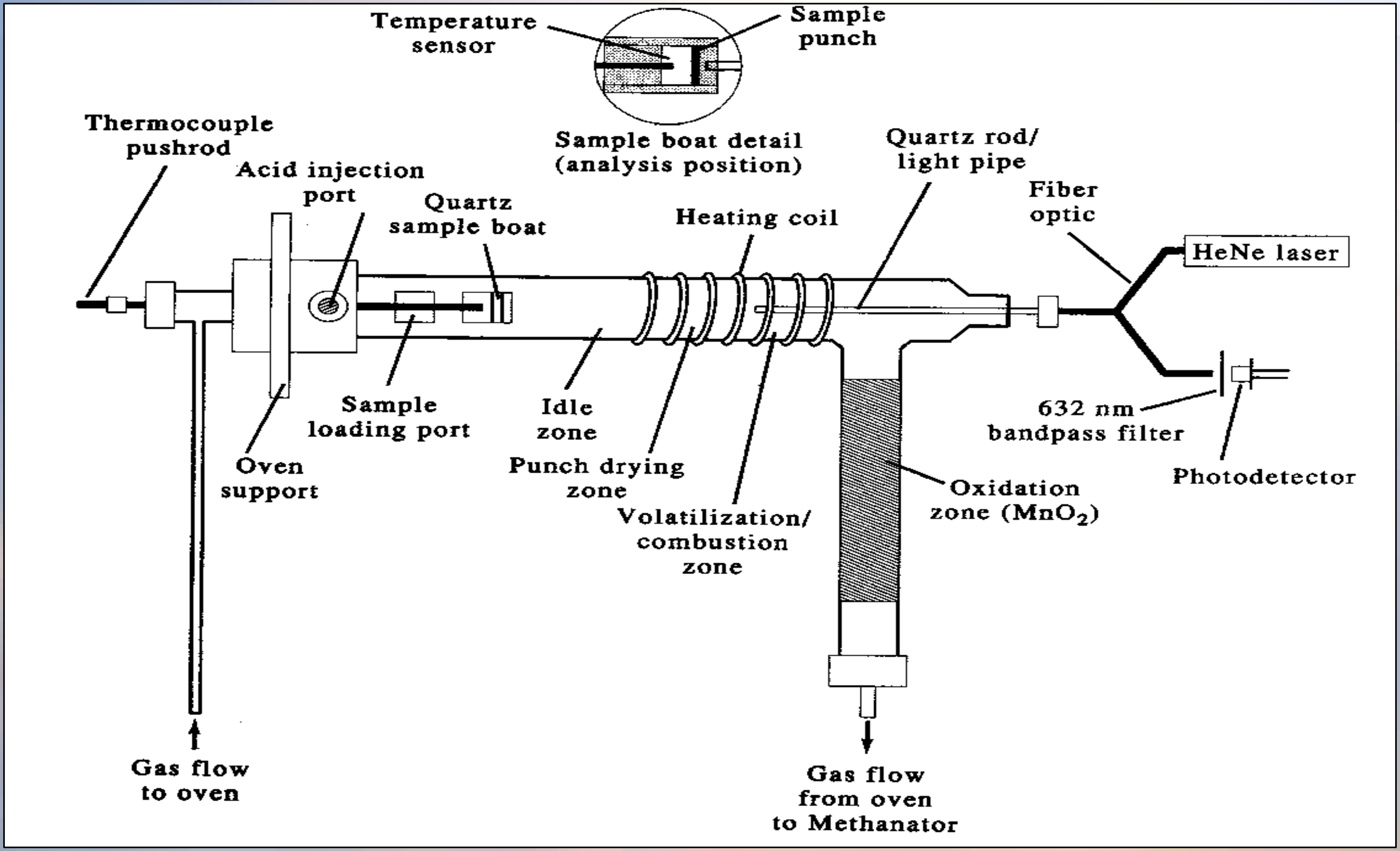
Thermal volatilization methods are based on temperature and atmosphere composition. **Sample temperatures** and **atmosphere composition** affect the distribution of carbon fractions

- How accurate does the oven temperature reflect the sample temperature?
- Can the composition of the atmosphere be maintained within the oven?

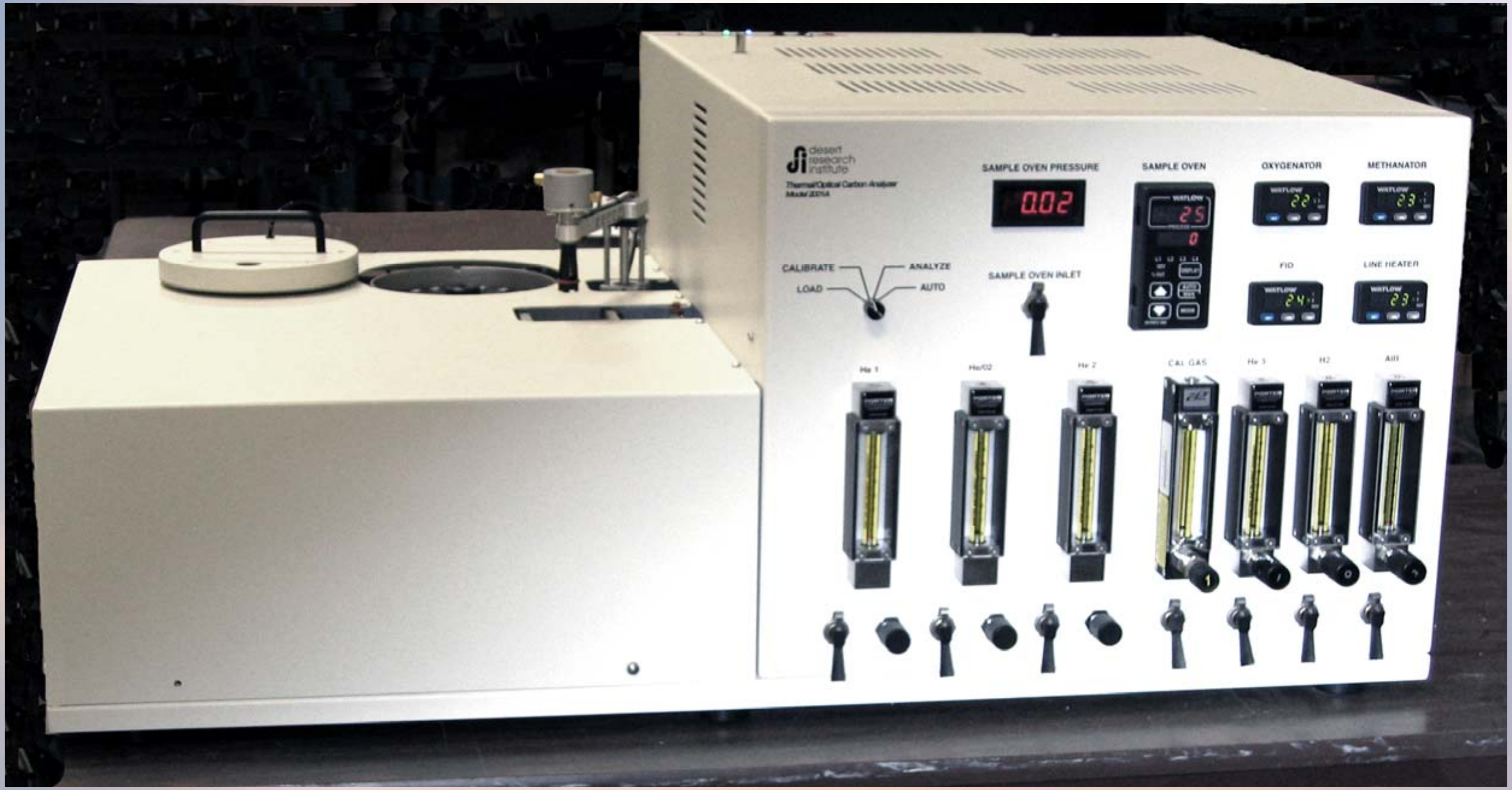
Original OGC/DRI Thermal Optical Analyzer (1986)



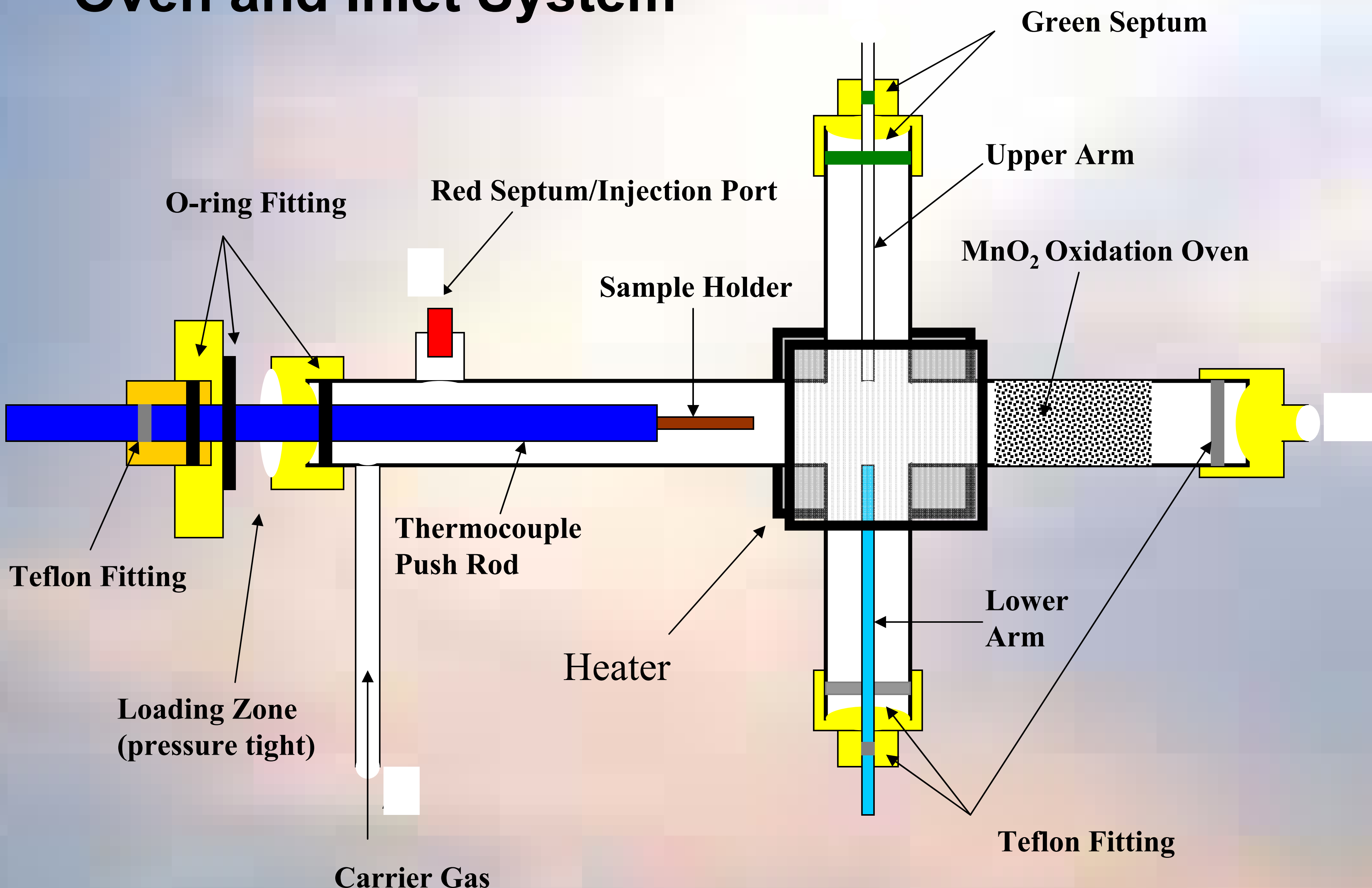
Configuration of DRI/OGC Analyzer



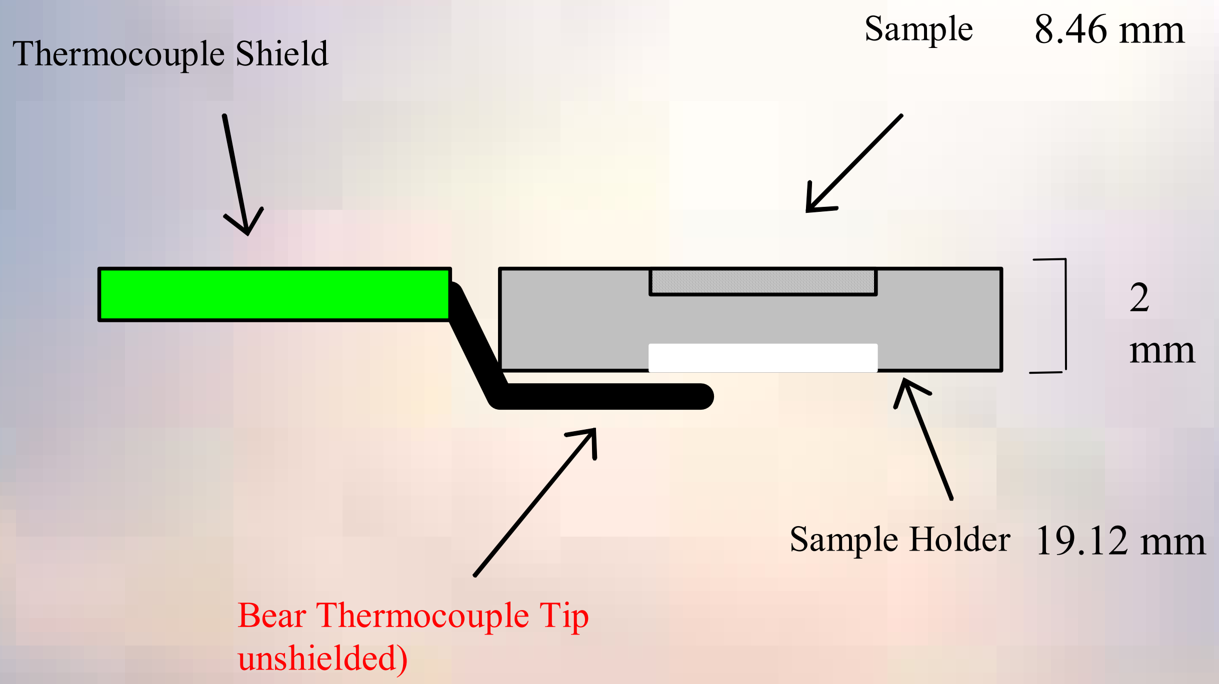
DRI Model 2001A Thermal/Optical Carbon Analyzer (2005)

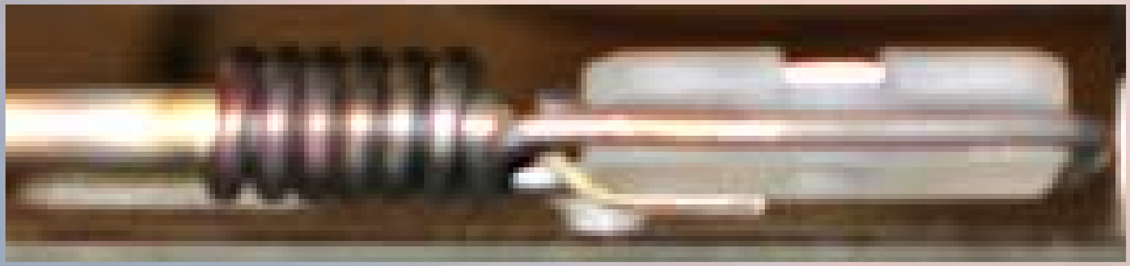


Configurations of DRI Model 2001: Sample Oven and Inlet System



Configuration of DRI Model 2001: Sample Holder and temperature sensor





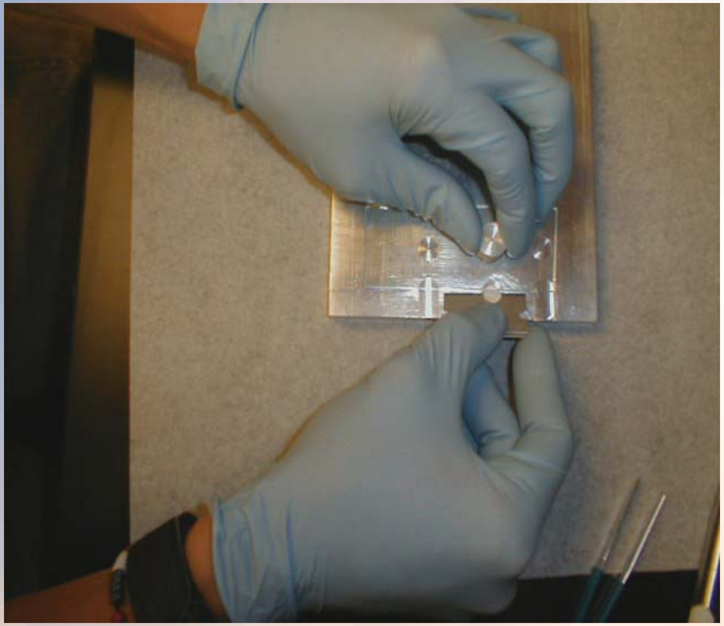
Why is it necessary to locate the temperature sensor at the sample?

- To provide accurate sample temperature because carbon fractions are temperature dependent
- Source attribution depends on carbon fractions
- Temperature inaccuracy affects data uniformity and reproducibility from analyzers within a laboratory
- It also affects interlaboratory comparison results

Potential Temperature Biases in Carbon Analysis

- Sample oven inhomogeneity
- Distance between thermocouple and filter punch
- Different thermal properties of sample and temperature sensor
- Thermocouple response time

Temperature Calibration



Slice the quartz-fiber filter punch in half.

Choose Tempilaq melting point standards (+ 2%, NIST traceable

Temperature Calibration (cont'd)

Quartz disc

Glass disc

Use diamond knife to cut glass discs or purchase manufactured quartz discs

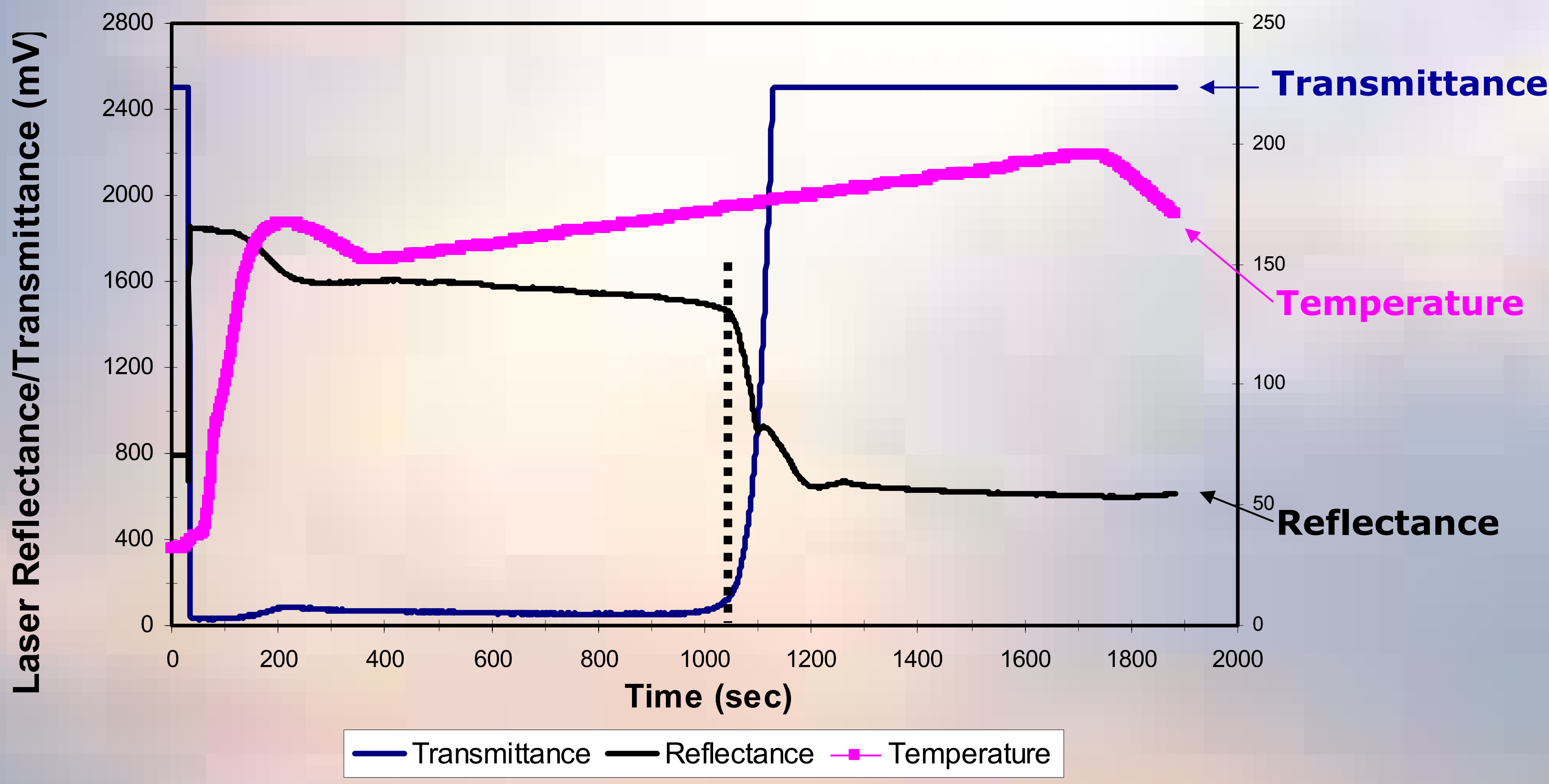
- **Micro cover glass** (Ted Pella, Inc, Redding California, USA)
- **Quartz disc** (Continental Glass, Burbank, USA); **Diamond knife** (Alltech, Deerfield, Illinois, USA)

Temperature Calibration (cont'd)

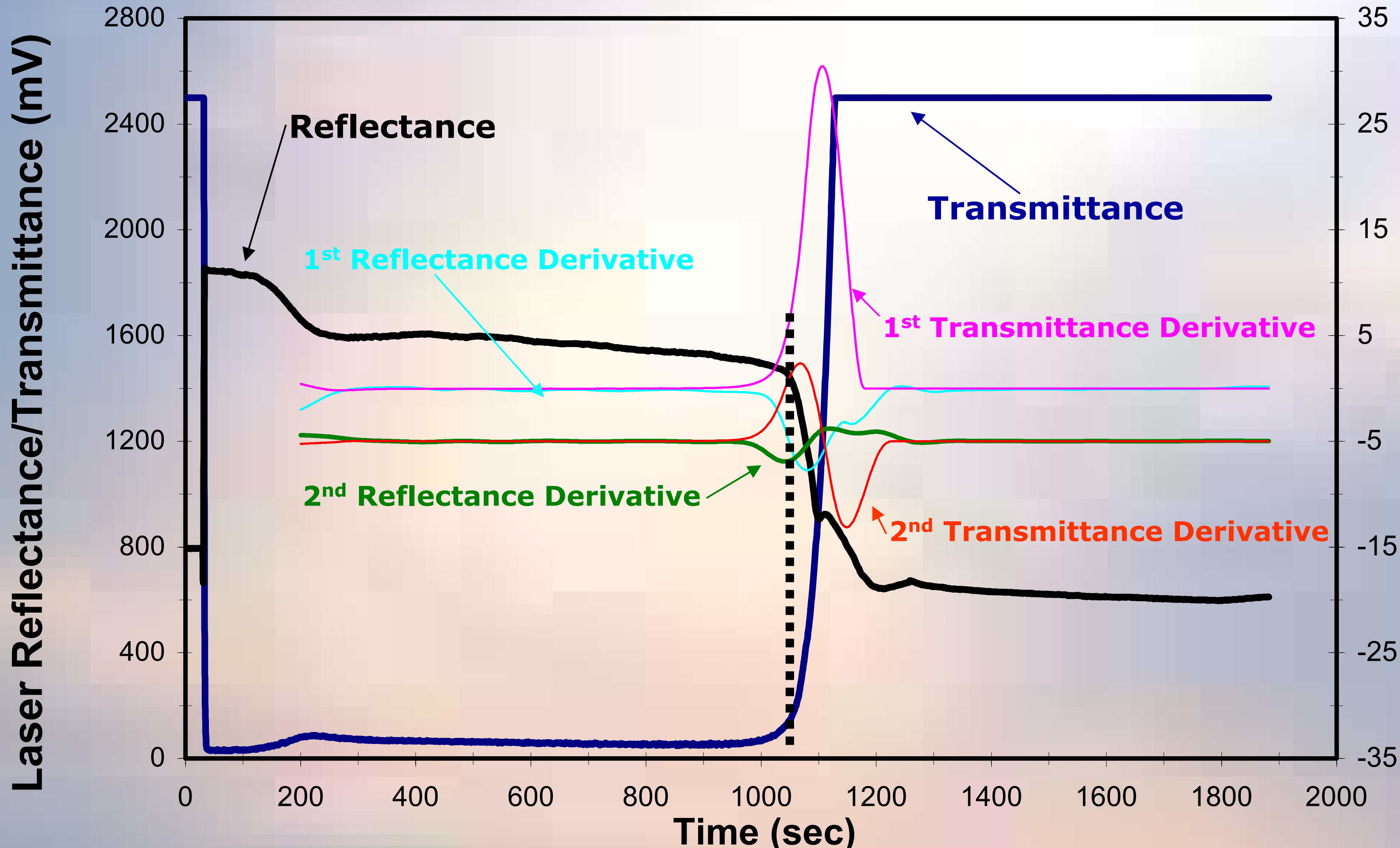
Apply Tempilaq on the glass or quartz disc, air dried, and cover with quartz filter punch

Press and ensure adherence of glass or quartz discs on Tempilaq sample

Response of Reflectance and Transmittance to Temperature

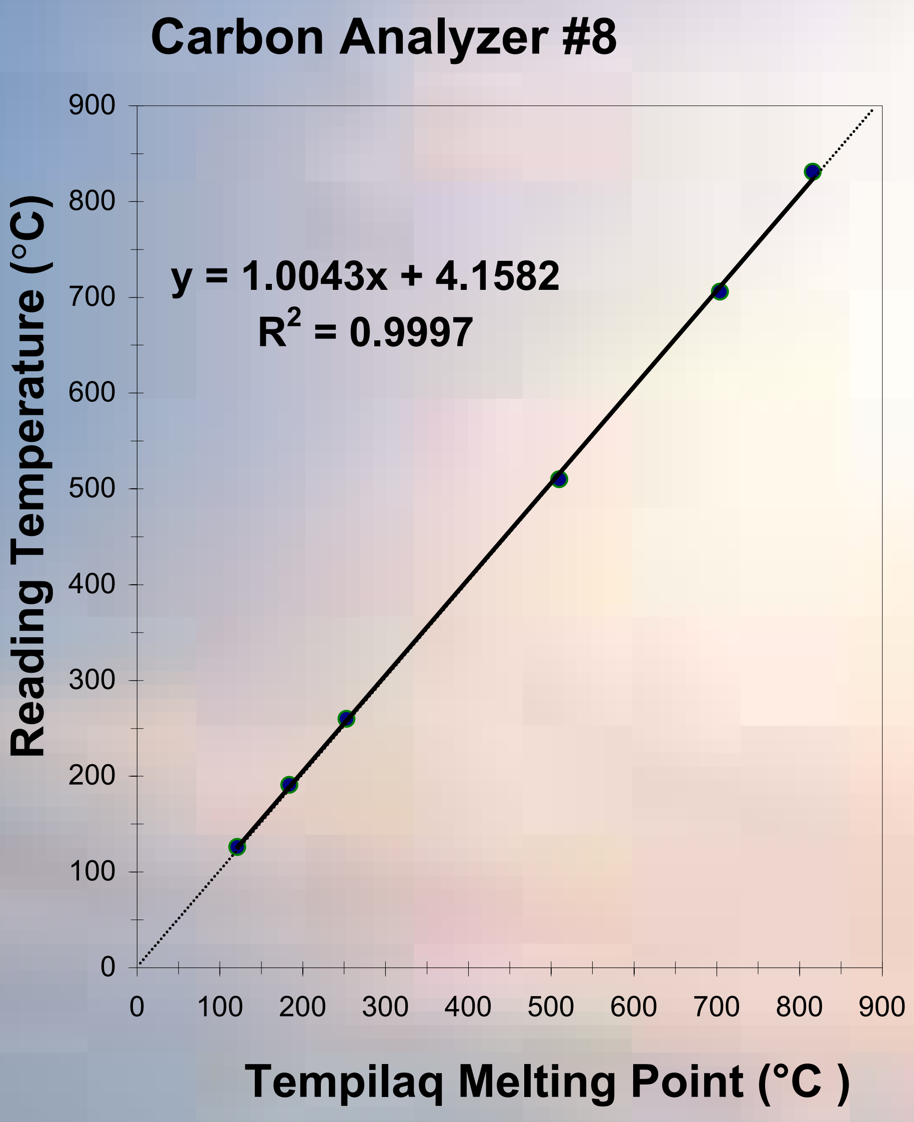


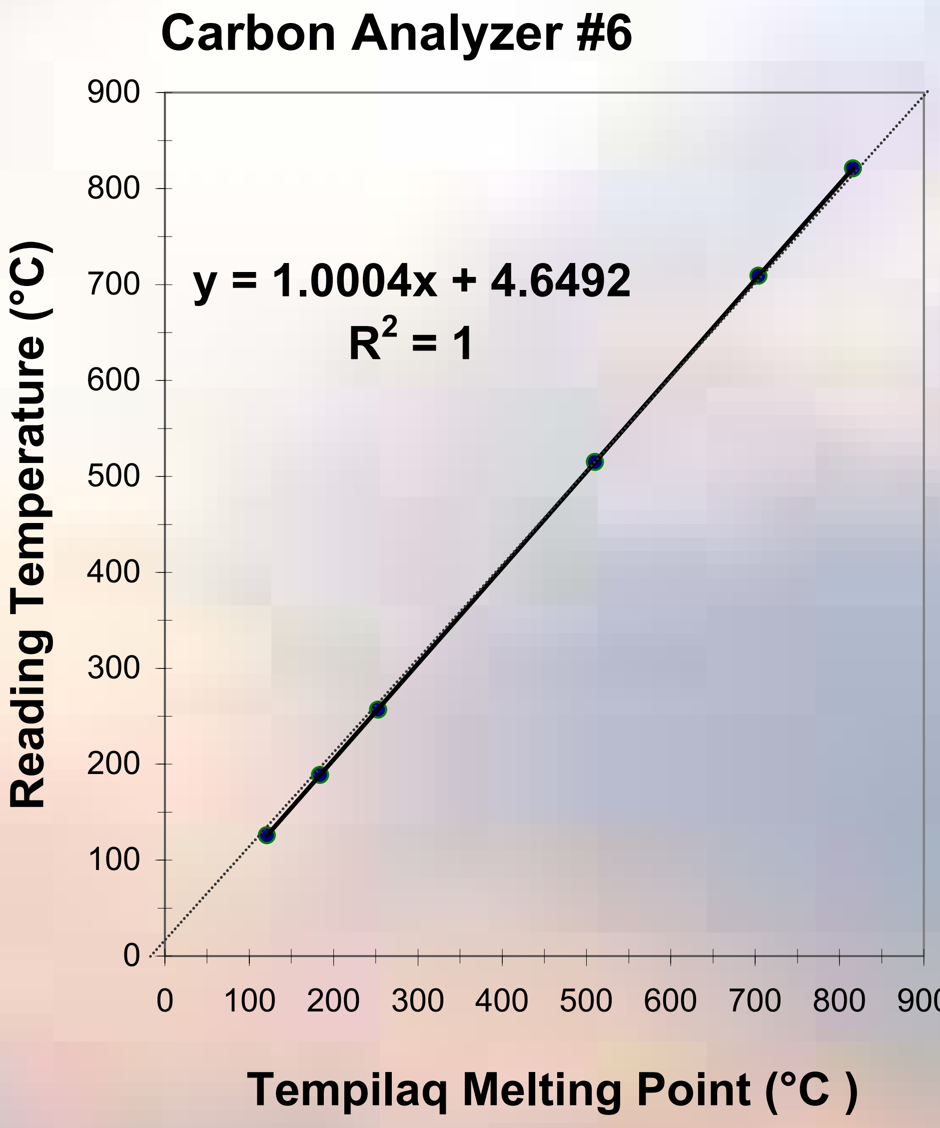
Use Second Derivative to Estimate the Melting Point



(Tempilaq's melting point 184 ± 2 ºC)

Example of Temperature Calibration

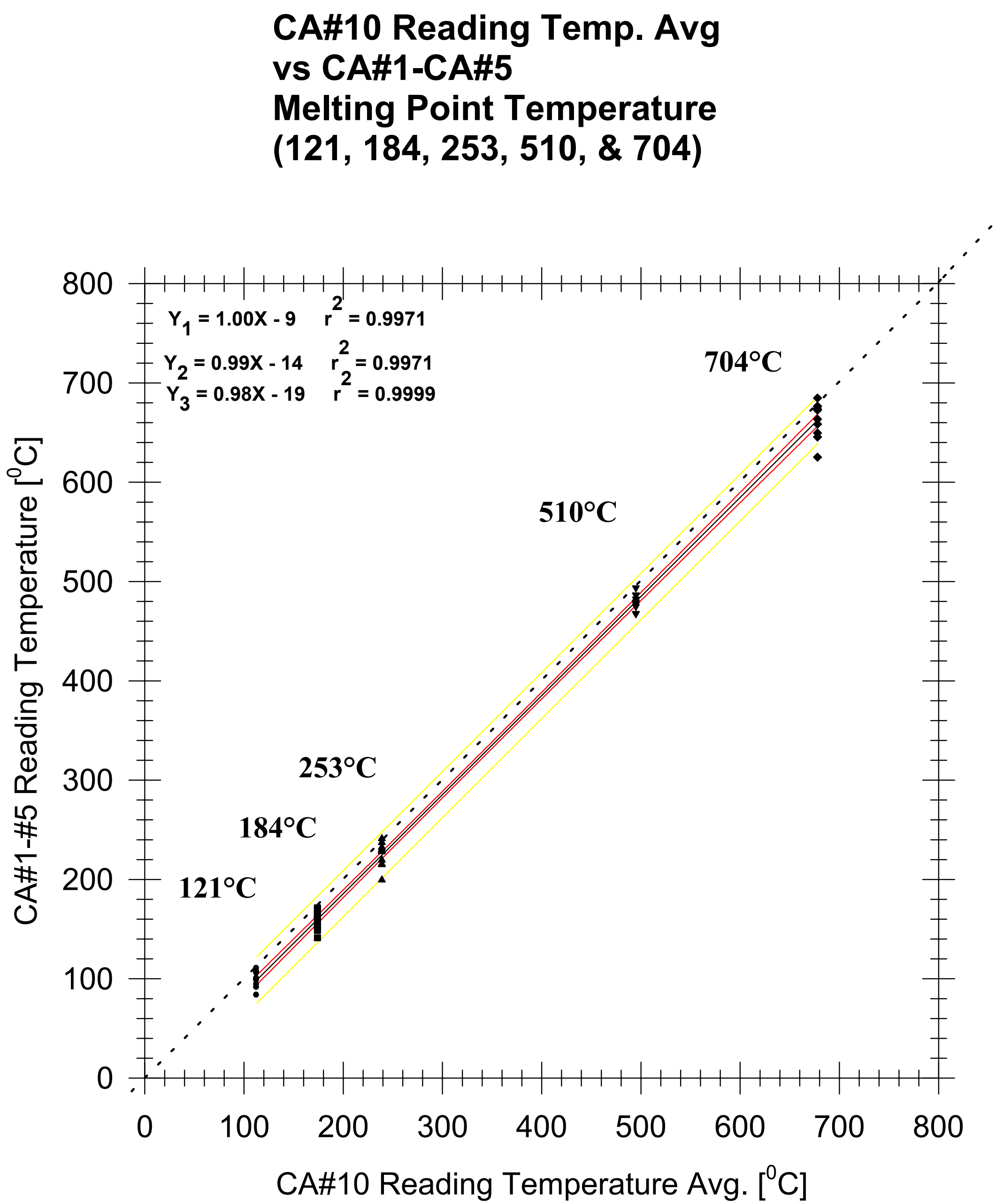




Temperature Variations of 2–15 ºC between Carbon Analyzers

Tempilaq Temperature (°C)	DRI 2001 CA #8 (°C)	ΔT (°C)	DRI 2001 CA #6 (°C)	ΔT (°C)
121 ± 2	125 - 127	-6 - -4	113 -115	6 - 8
184 ± 2	190 - 192	-8 - -6	175 - 179	5 - 9
253 ± 3	258 - 262	-9 - -5	246 – 248	5 - 7
510 ± 4	509 - 510	-0.5 – 0.5	499 – 500	10 - 11
704 ± 6	705 - 706	-2 – -1	697 – 700	4 - 7
816 ± 9	830 – 831	-15- -14	816 - 818	-2 - 0

Temperature calibration helps to identify problems to be corrected



DRI/OGC Analyzers

- A temperature variation of 30 – 50 °C is found across 5 DRI/OGC carbon analyzers.
- DRI/OGC analyzers operate at higher sample temperatures than DRI 2001 carbon analyzer even though the temperature sensor gave identical temperatures.

Practical Application:

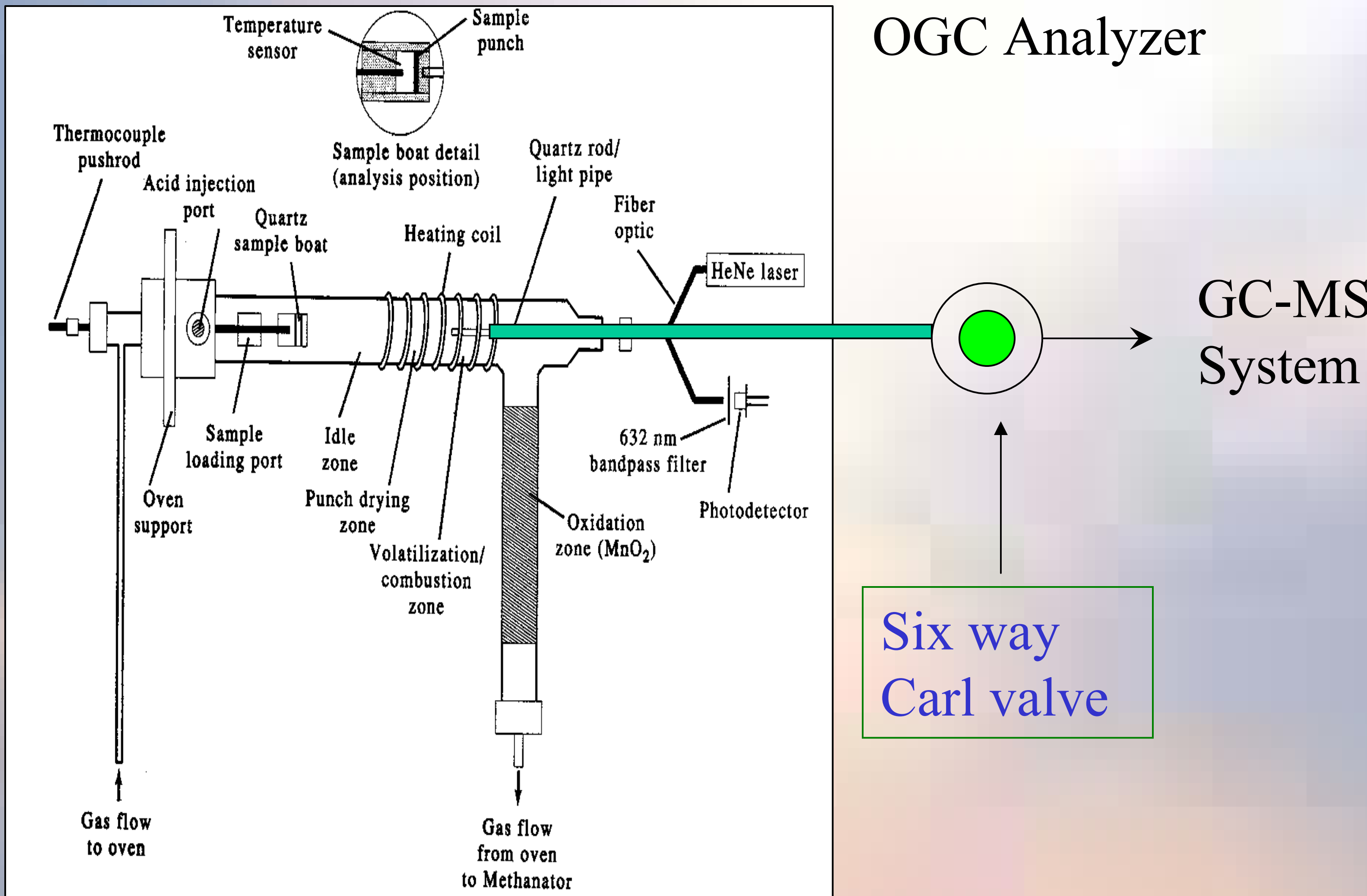
Temperature calibration equation can be applied in the analyzer to produce accurate sample temperatures

How does trace oxygen in the carrier gas affect carbon analysis?

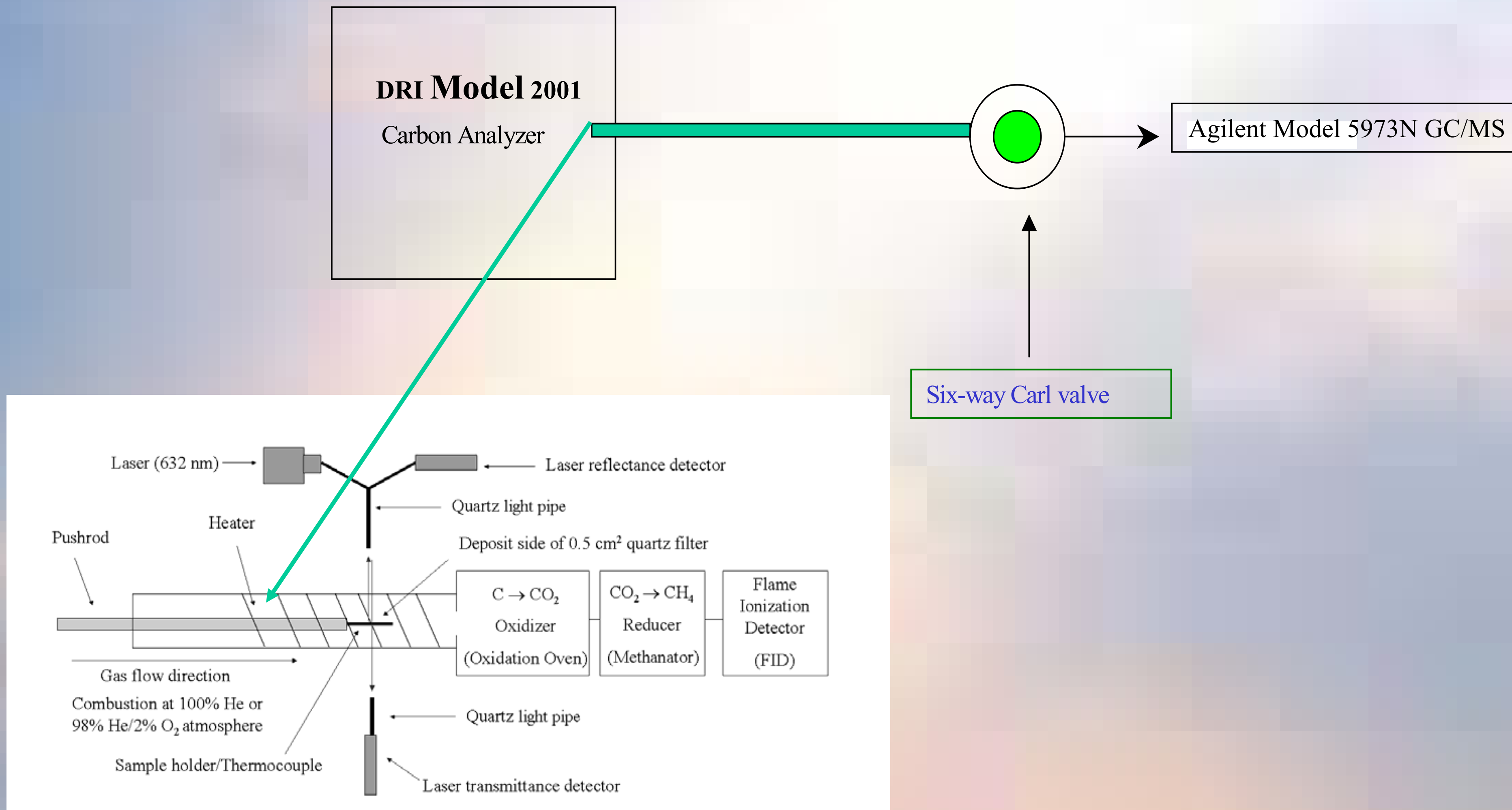
Potential Origins of Oxidant in Helium Carrier Gases

- Carrier gas is not pure.
- Diffusion of ambient air into the analyzer oven
- Residual air in the oven after purging
- Decomposition of MnO_2 in the oxidation oven

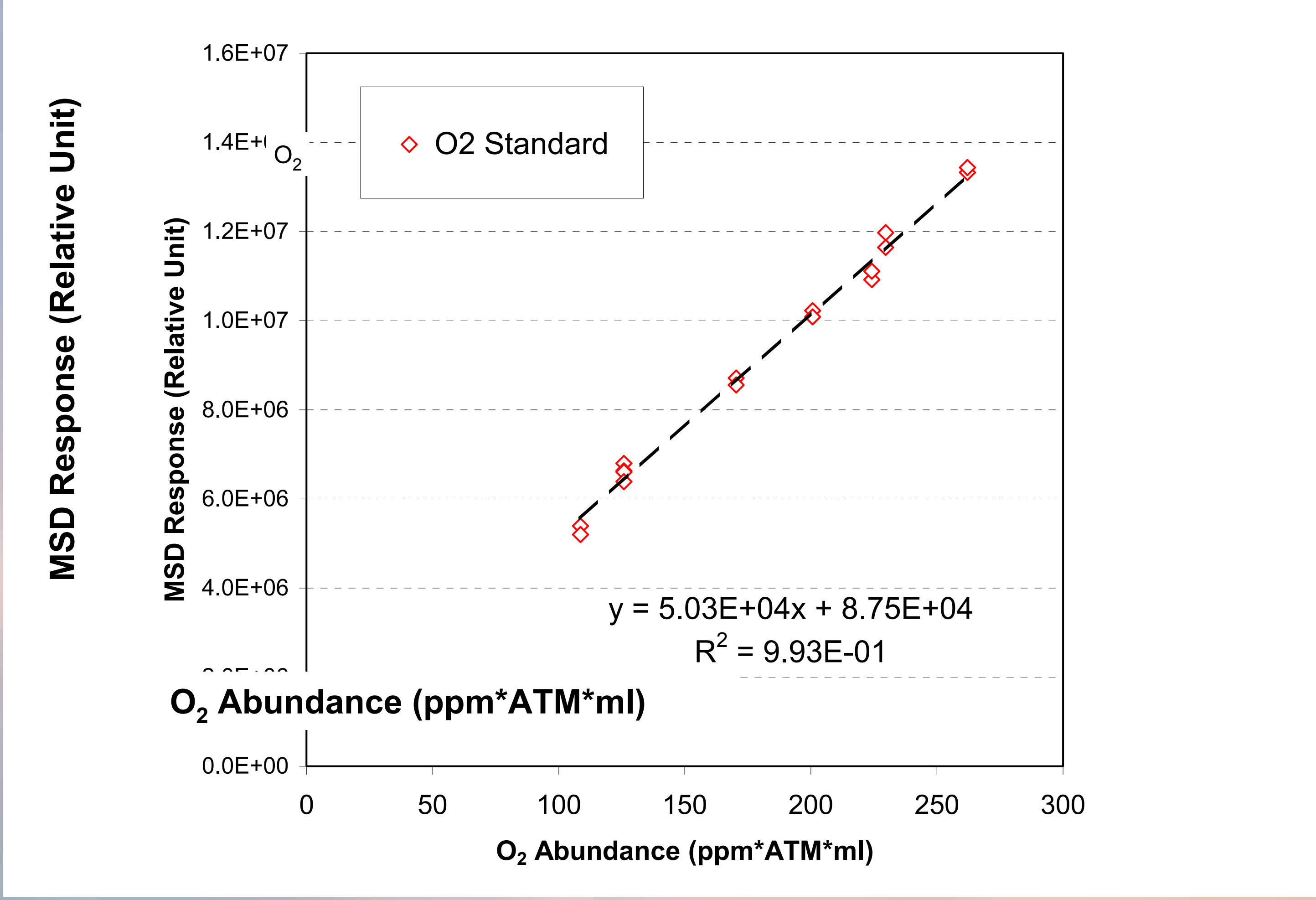
Quantify oxygen in helium atmosphere



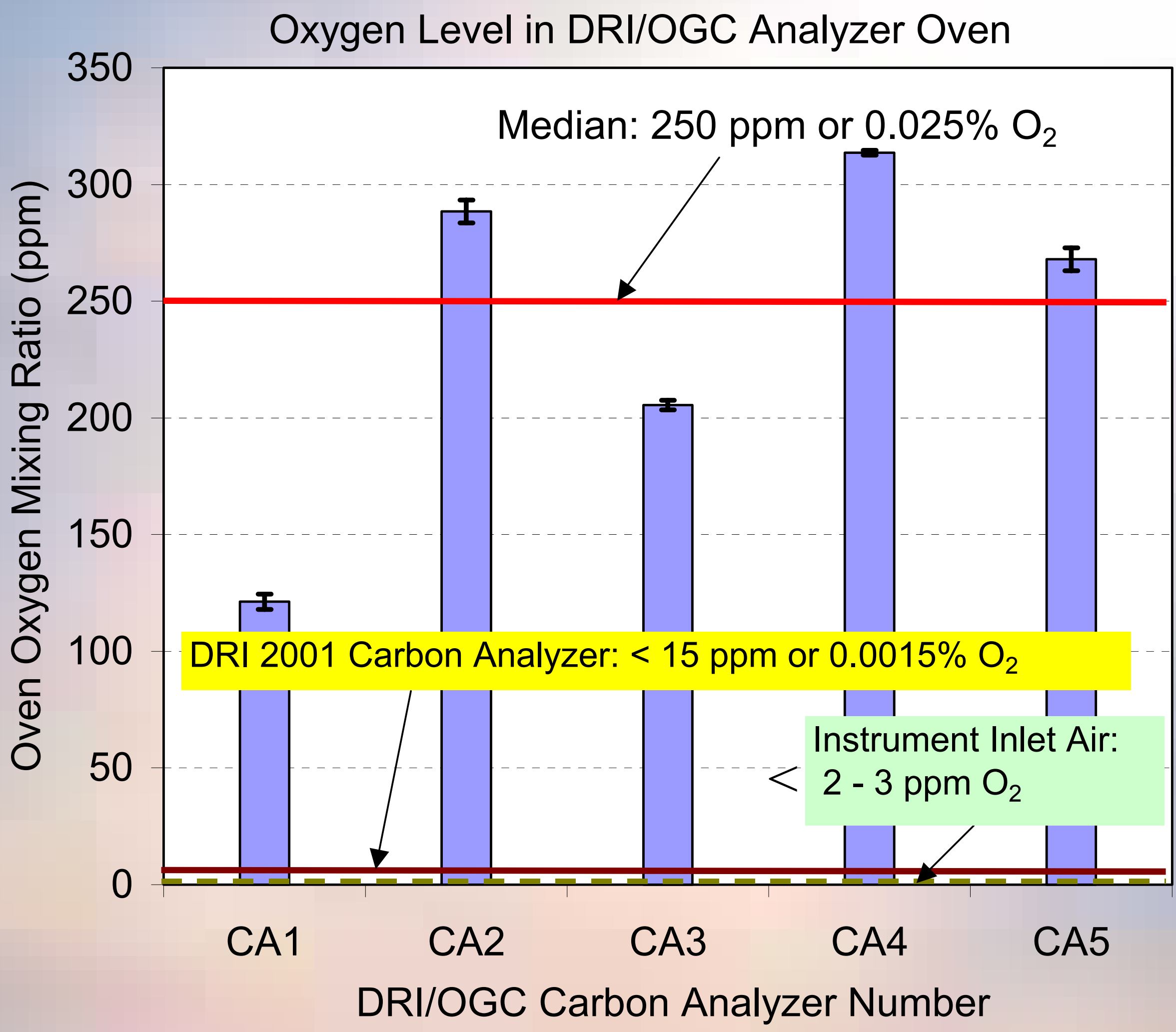
Use GC/MS to Detect Low-Level O_2 in Helium



GC/MS Shows Linear Response for Low-Level O_2



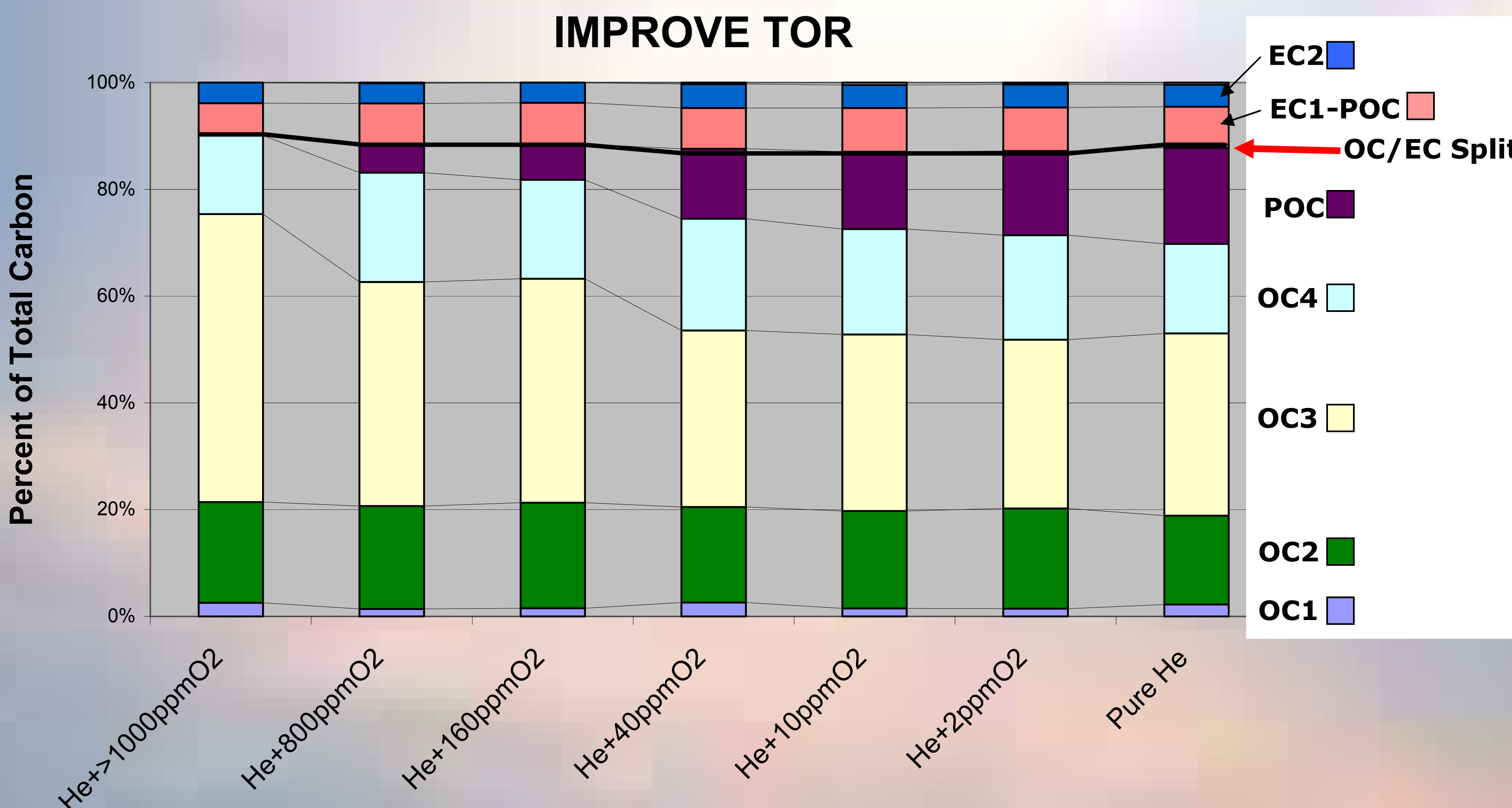
Trace Oxygen Comparison



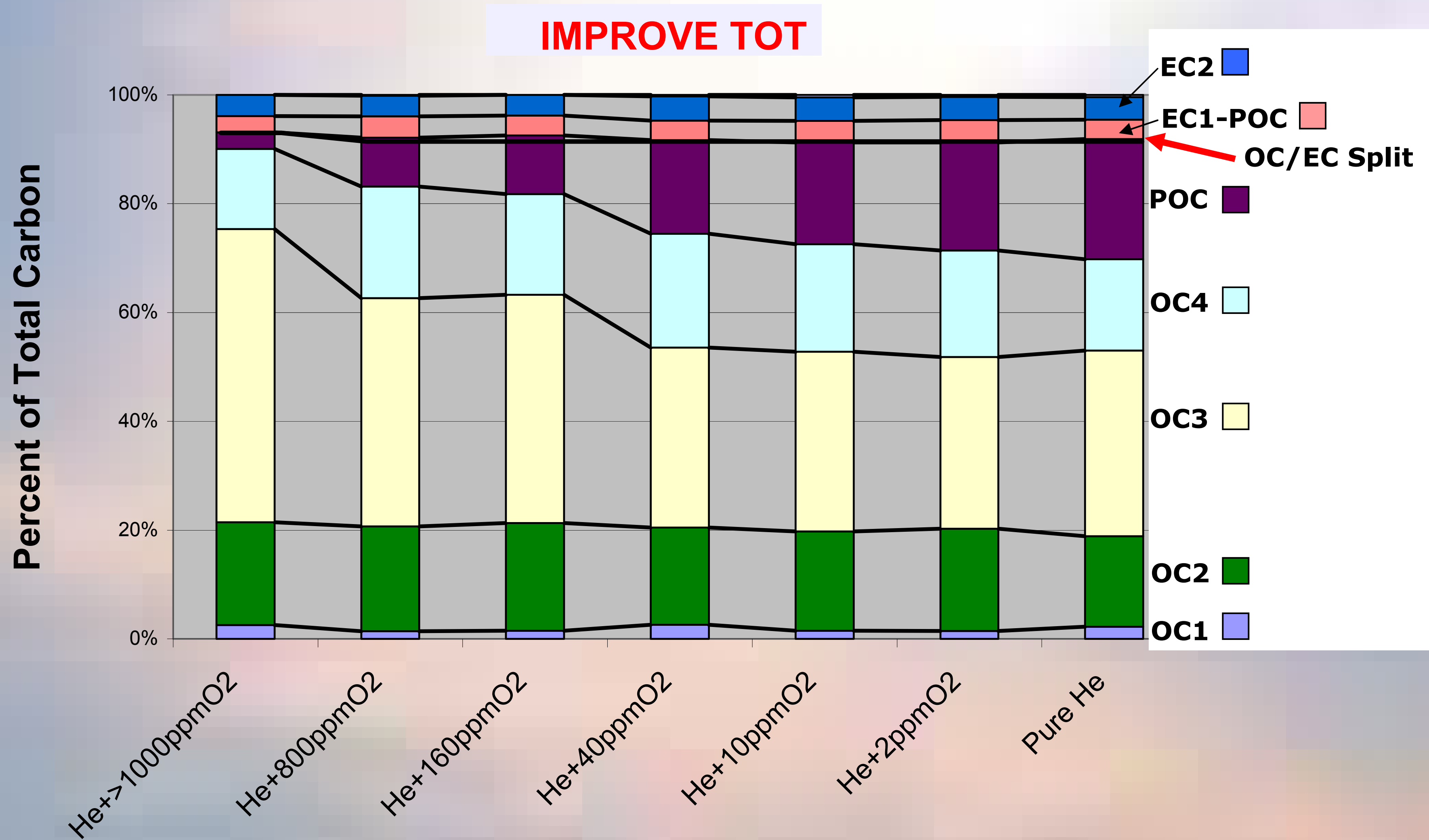
The trace oxygen level in the DRI/OGC analyzer is not well controlled (as measured in 4/2004).

How much O_2 before the carbon results are effected?

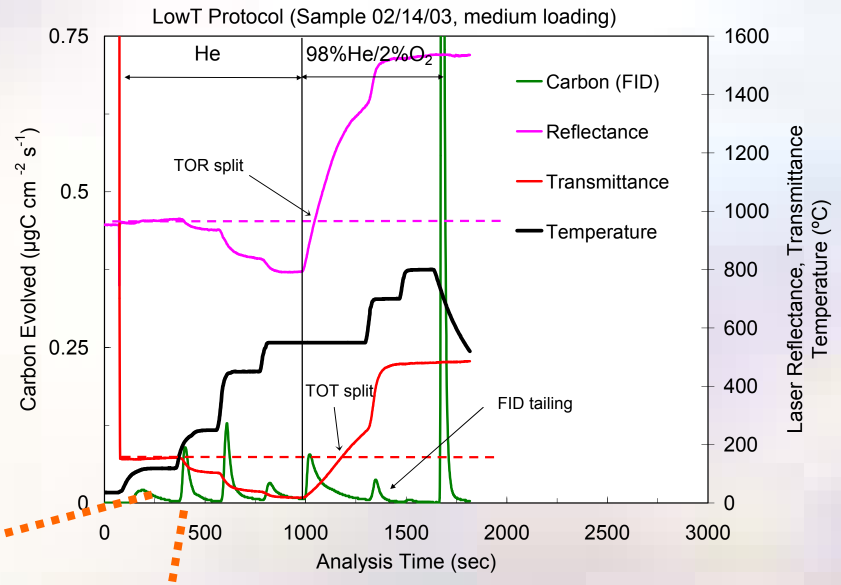
IMPROVE OC/EC split not affected by <800ppm O2 in He. Carbon fractions not affected by O2<40 ppm

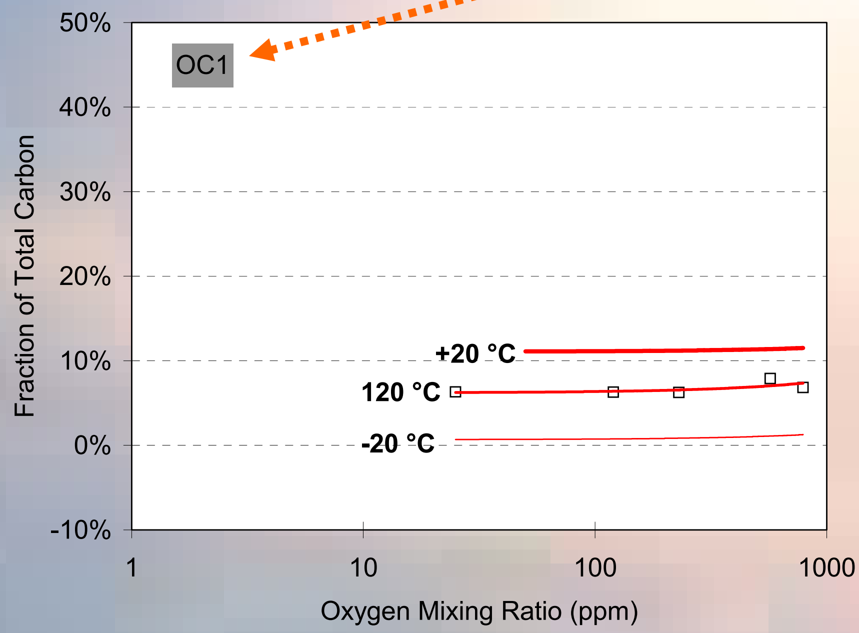


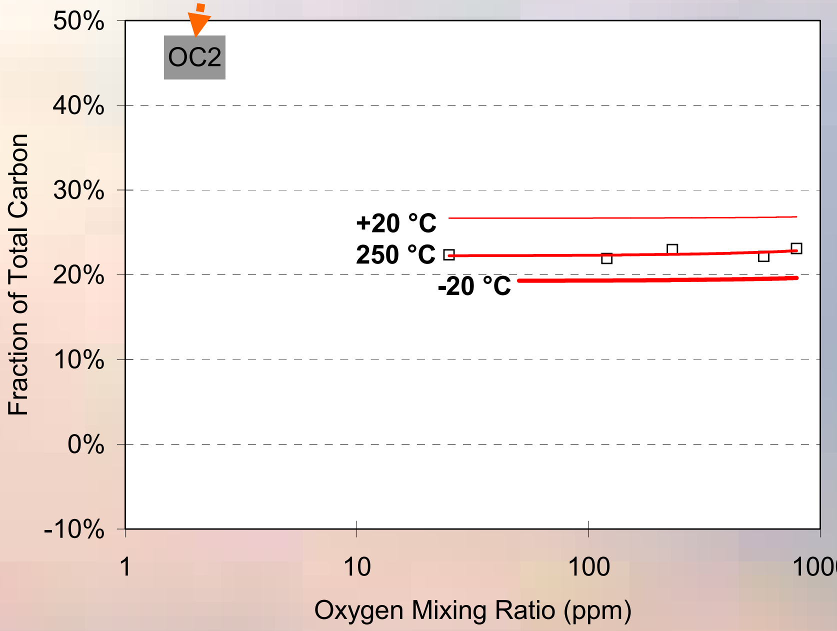
Introducing O_2 (< 800 ppm or 0.08%) in Helium Does Not Affect OC/EC Split by Transmittance



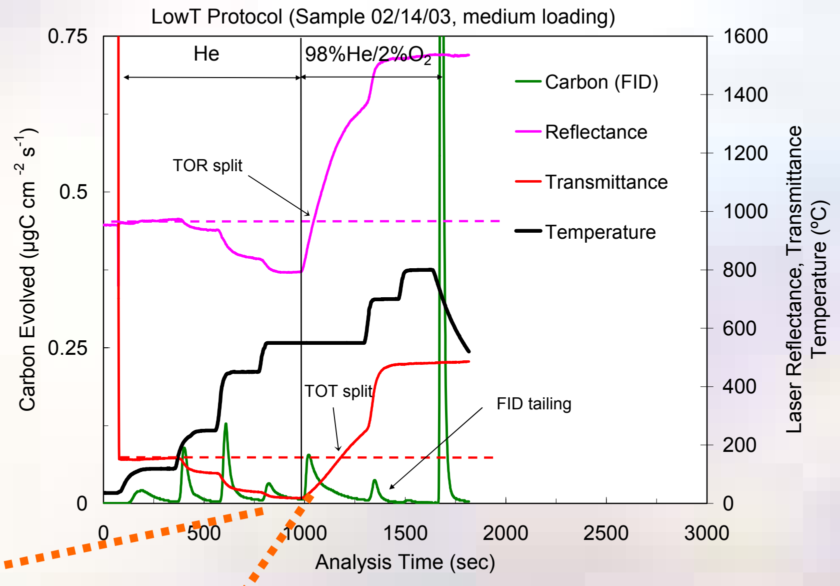
Low Temperature OC Fractions are More Sensitive to Temperature than to Analysis Atmosphere

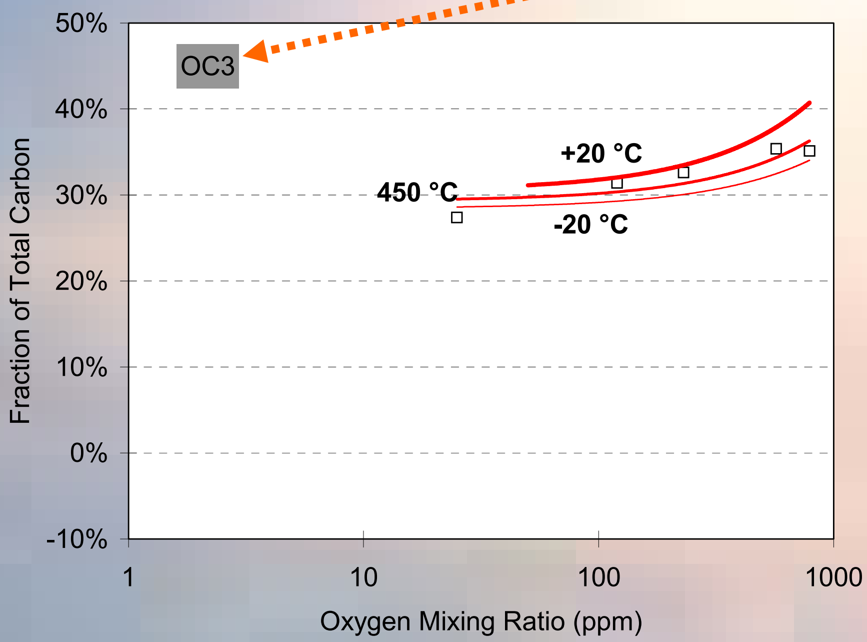


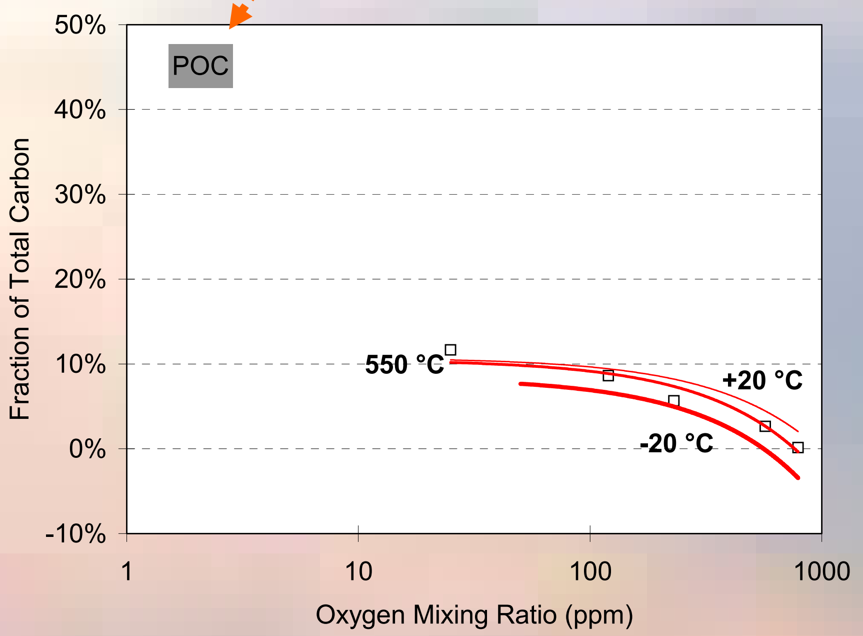




OC3 and charred OC are More Sensitive to Analysis Atmosphere than to Temperature

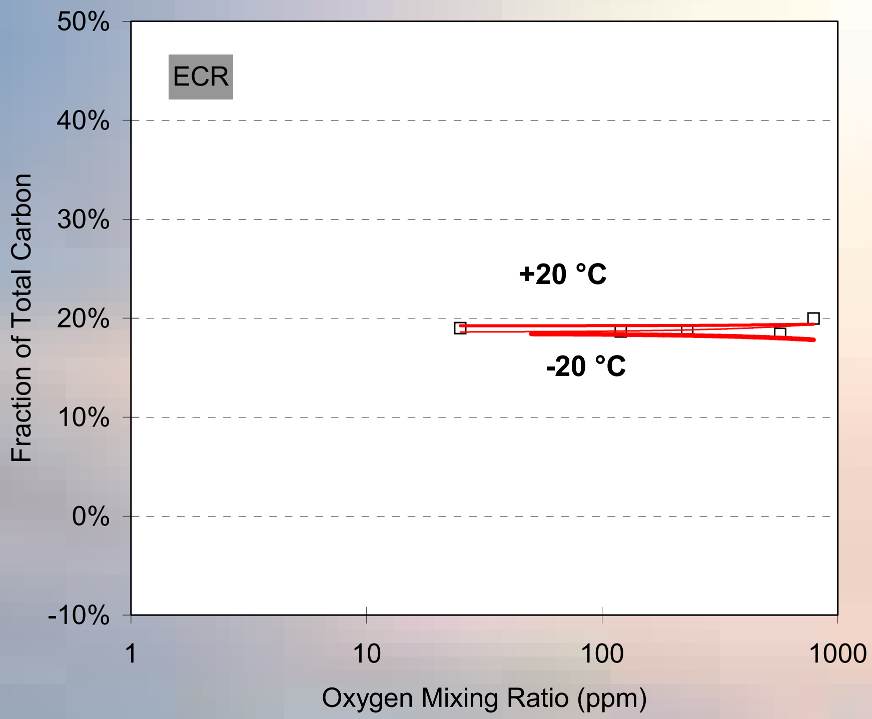




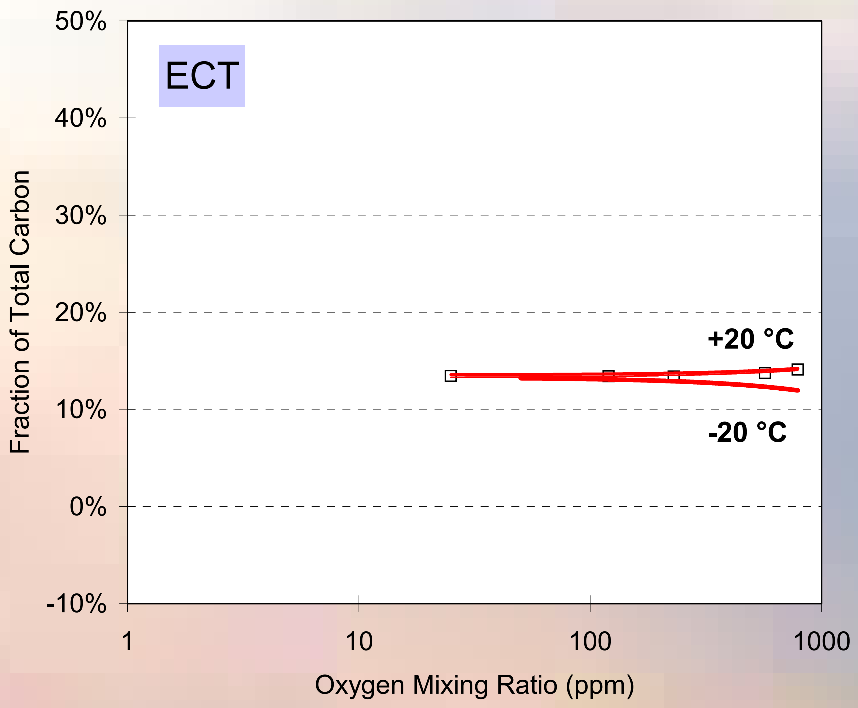


EC and OC don’t vary with temperature or atmosphere They do differ between TOR and TOT corrections

Reflectance Correction



Transmittance Correction



Summary of Trace O_2 Effects

- Model 2001 shows insignificant level of O_2 present in the He carrier.
- Up to ~800ppm of O_2, the OC/EC split is unaffected using IMPROVE-TOR or IMPROVE-TOT,
- OC-1 and OC-2 are unaffected by O_2 , but they are temperature sensitive
- OC-3 and OC-4 and POC fractions are affected with increasing O_2
- EC and OC measured through optical charring correction is more robust, less sensitive to the analytical conditions.
- TOR and TOT give different EC/OC split.

What is the IMPROVE-A protocol?

The systematic evaluation of temperature and oxygen effects in analyzers resulted in adoption of IMPROVE-A protocol in IMPROVE Network.

- IMPROVE-A - Plateau temperatures are adjusted so that the new analyzer will produce carbon fractions similar to the original OGC analyzers. This will allow a smooth transition from the aging units to the Model 2001.
- OC in He – 140, 280, 480, 580
- EC in O_2/He – 580, 740, 840

Should others switch to IMPROVE-A?

Some simple guidelines – KF’s perspectives

- Doesn’t matter if only OC/EC values are of interest. Both protocols give identical results
- Switch over if you are interested in comparing carbon fractions to the IMPROVE database.
- Use IMPROVE-A if your are starting or have not compiled a large database of your own.

Applications- Examples

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 110, D03203, doi:10.1029/2004JD005244, 2005

Characterization of airborne carbonate over a site near Asian dust source regions during spring 2002 and its climatic and environmental significance

J. J. Cao,[1] S. C. Lee,[2] X. Y. Zhang,[1] Judith C. Chow,[3] Z. S. An,[1] K. F. Ho,[2] John G. Watson,[3] Kochy Fung,[4] Y. Q. Wang,[1] and Z. X. Shen[1]

Received 16 July 2004; revised 20 October 2004; accepted 26 November 2004; published 8 February 2005.

Particulate carbonates:

- A filter punch is acidified with 25% H_3PO_4
- The CO2 released is measured as CH_4 in the analyzer.

Larger filter aliquots can be used to increase carbonate detection sensitivity

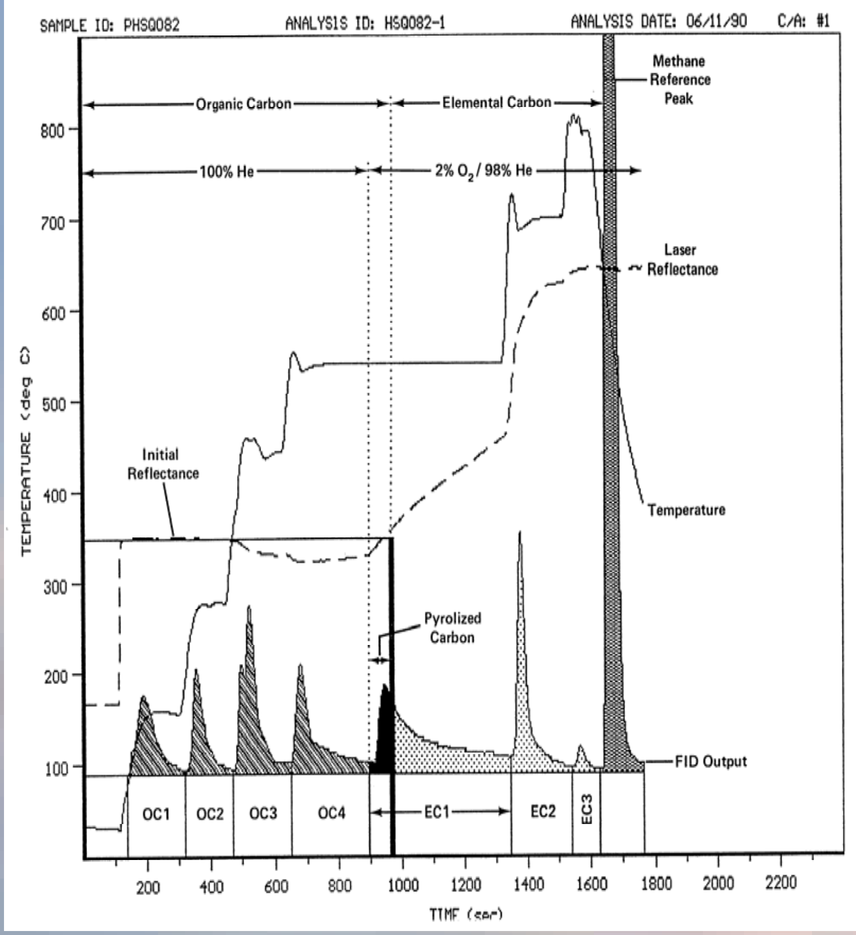
Water soluble organic carbon

- Need a platinum boat for the aqueous extract
- Results relate to the polar organic compounds present in the aerosol
- Secondary organic aerosol and impact of cooking increase the level of this fraction.

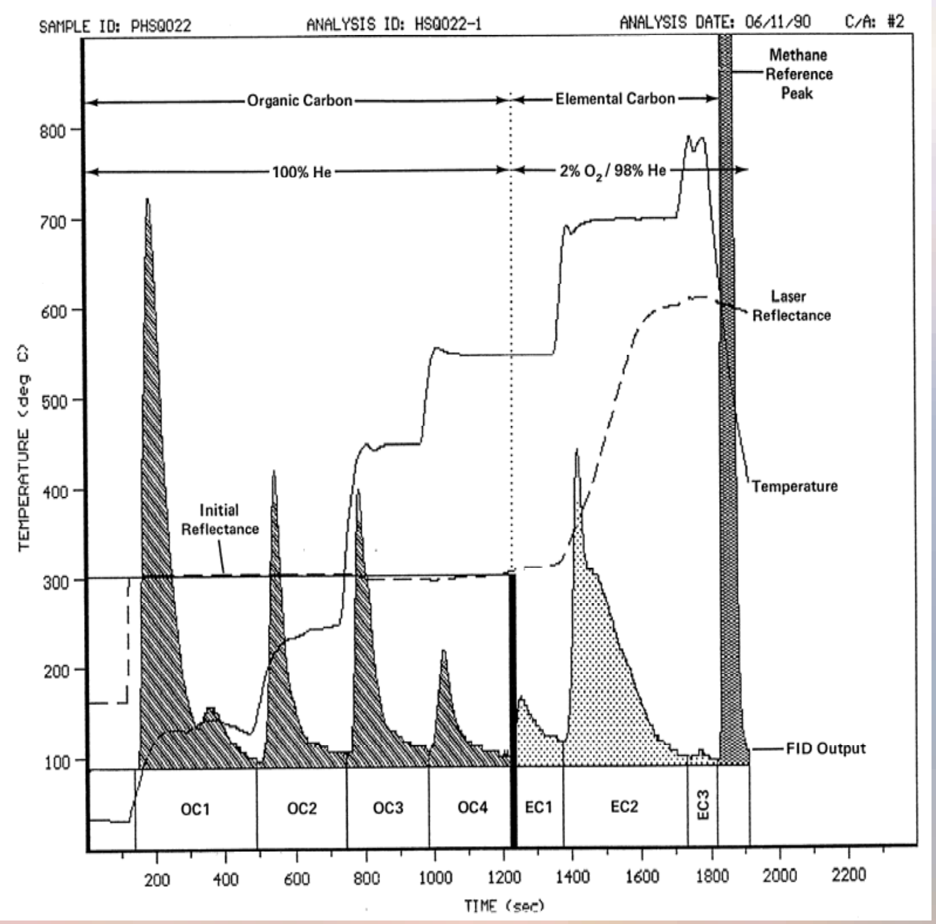
Source Properties can be Operationally Defined

(Thermally evolved carbon fractions, Watson et al., 1994)

Gasoline-fueled vehicles



Diesel-fueled vehicles



Source Apportionment

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* 55:1456–1463

Improving Source Apportionment of Fine Particles in the Eastern United States Utilizing Temperature-Resolved Carbon Fractions

Eugene Kim

Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY

Philip K. Hopke

Department of Chemical Engineering, Clarkson University, Potsdam, NY

- Need source profiles
- Multivariate Receptor Modeling

Complimentary Analysis Techniques- Ongoing research

- Filter thermal desorption-GC/MS to generate source profiles and examine the profiles of samples from receptor.

  Identify peaks that are consistent within a source type, but differ between source types.

  Technique is less time consuming than solvent extraction approach to give more information for source apportionment.

- The carbon fractions can be better defined by additional temperature plateaus.

Thank you !

It’s been my pleasure to speak with you.